昭和33年12月25日　昭和36年12月8日 印刷 [毎月1回
第3種郵便物認可　昭和36年12月15日 発行 15日発行]

OHIO STATE UNIVERSITY
FEB 21 1962
LIBRARY

# BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

Vol. 34 No. 12 December 1961

## CONTENTS

**General and Physical**

Normal Vibrations of Dimethyldimethoxysilane . . . . . T. TANAKA 1752
Chemical Use of the Absorption of Soft $\gamma$-Rays, $\beta$-Ray-excited and X-Rays and K-Capture X-Rays. I. Improvement in Fundamental Technique and Introduction of a Differential Absorption Method . . . . . T. NOZAKI 1769
Visible Absorption Spectra of 1,3,5-Trinitrobenzene and its Derivatives in Aqueous Alkaline Acetone. . . . . T. ABE 1776
Sur la Dissolution des Minerais Sulfurés en Divers Milieux. V. Dissolution de la Sphalérite. . . . . M. ICHIKUNI et H. KAMIYA 1780
Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. I. Preparation of Cobalt Soap by Metathesis . . . . . H. KAMBE 1786
Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. II. Compositions of Cobalt Soaps . . . . . H. KAMBE 1790
Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. III. Spectrophotometric Specifications of Colors of Cobalt Soaps . . . . . H. KAMBE 1794
Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. IV. Ionic Nature of Cobalt Soaps, Revealed in Infrared Absorption Spectra and Magnetic Susceptibilities . . . . . H. KAMBE and I. MITA 1797
Statistical Thermodynamics of Solutions of Optically Active Substances. II. Solubility of *d*- and *l*-Isomers in Optically Active Solvents . . . . . K. AMAYA 1803
Liquid-Vapor Equilibrium of Isotope Mixture under Centrifugal Force . . . . . K. AMAYA 1807
The Raman Spectra of 1,3,5-Trichlorobenzene and 1,3,5-Trichlorobenzene-$d_3$ . . . . . S. SAËKI 1851
Raman Spectra of 1,2,4,5-Tetrachlorobenzene and 1,2,4,5-Tetrachlorobenzene-$d_2$ . . . S. SAËKI 1858
Mass-spectrometric Study on Ionization and Dissociation of Formaldehyde, Acetaldehyde, Acetone and Ethyl Methyl Ketone by Electron Impact . . . . . I. KANOMATA 1864

**Analytical and Inorganic**

A New Method for the Determination of Boron by Spectrophotometry with Pyrocatechol Violet . . . . . K. HIIRO 1743
A New Method for the Spectrophotometric Determination of Boron with Quercetin. . K. HIIRO 1748
Thermodynamic Studies on Cobalt Complexes. VIII. Some Information about Diaquotetramminecobalt(III) Complexes and Thermal Dissociation of the Corresponding Chloride . . . . . M. MORI, R. TSUCHIYA, S. TAKEMURA and E. MATSUDA 1757
Thermodynamic Studies on Cobalt Complexes. IX. Chemical Equilibrium between Diaquotetramminecobalt(III) Complex and Oxalate Ion. . . . M. MORI, R. TSUCHIYA and E. MATSUDA 1761
Chemical Studies on Radioactive Indicators. XXIV. Separation of Rhenium from Technetium by the Distillation Method . . . . . M. KOYAMA 1766
Adsorbabilities of Diacidotetrammine Type Cobalt(III) Complex Ions on a Cation Exchanger . . . . . M. MORI, M. SHIBATA and K. HORI 1809

*(Continued on inside cover)*

Published by the Chemical Society of Japan

# THE CHEMICAL SOCIETY OF JAPAN
## (NIPPON KAGAKUKAI)

**Founded in 1948**

Successor to the former Chemical Society of Japan founded in 1878 and to the Society of Chemical Industry, Japan founded in 1898.



### OFFICERS

San-ichiro MIZUSHIMA, *President*, Director of Tokyo Research Institute Yawata Iron and Steel Co., Ltd.
Yoshikazu HACHIHAMA, *Vice-President*, Osaka University
Kenji IWAMOTO, *Vice-President*, The University of Gunma
Yonezo MORINO, *Vice-President*, The University of Tokyo
Sojiro OKA, *Vice-President*, The University of Tokyo
Hiroshi SOBUE, *Vice-President*, The University of Tokyo

### BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

*Editor:* Tadao SHIBA, Tokyo Institute of Technology, Tokyo
*Assistant Editor:* Tadashi SUEHIRO, Gakushuin University, Tokyo
*Editorial Board:*

| | | |
|---|---|---|
| Yoshié BANSHO | Hidehiro GOTÔ | Keniti HIGASI |
| Yoshimasa HIRATA | Hiroo INOKUCHI | Tatsujiro ISHIMORI |
| Tadashi KAMIKUBO | Michio KOBAYASHI | Ichiro MIYAGAWA |
| Masazumi NAKAGAWA | Shigeru OAE | Shigeru OHASHI |
| Kazuo SATAKE | Syûzô SEKI | Osamu SIMAMURA |
| Yoshitada TOMODA | Iwao YASUMORI | Koshiro YOSHIOKA |


*(Continued from outside cover)*


Preparation and Absorption Spectra of the Cobalt(III) Complexes of Amino Acids . . . . . M. MORI, M. SHIBATA, E. KYUNO and M. KANAYA 1837
Studies on Metal Complex Species Using an Anion Exchange Resin. II. On the Adsorption of Silver from Nitrate Solution. . . . . H. WAKI 1842

**Organic and Biological**

The Beckmann Rearrangement of 1,2-Cyclohexane-dione Dioxime in Liquid Sulfur Dioxide . . . . . N. TOKURA, R. TADA and K. YOKOYAMA 1812
Studies of Violanthrone B. I. Reduction and Oxidation of Violanthrone B . . . . . J. AOKI 1817
Studies of Violanthrone B. II. Reduction of Isoviolanthrone B . . . . . J. AOKI 1820
Synthesis of Phenanthryl Phenyl Ethers . . . . . H. SUZUMURA 1822
Studies on Isoprenoide. XIII. Transformation of Pinene by the Action of Boron Trifluoride . . . . . K. NAGAI 1825
Alternant Conjugate Systems. I. Syntheses and Properties of Polytolans . . . . . S. MISUMI 1827
Alternant Conjugate Systems. II. Syntheses of Stereoisomeric *p*-Distyrylbenzenes and Related Compounds . . . . . S. MISUMI, M. KUWANA, K. MURASHIMA and M. NAKAGAWA 1833
Separations of Lutidines, Collidines and 2,3-Cyclopentenopyridines from Coal Tar Bases . . . . . H. SUZUMURA 1846

**Short Communications**

The Polymerization of γ-Methyl-L-glutamate-*N*-carboxyanhydride Initiated with Acetic Acid . . . . . T. OKUDA and S. SAKURAI 1872
Reduction of α-Pyrones with Complex Metal Hydrides . . . . . K. YAMADA, M. ISHIZAKA and Y. HIRATA 1873
Mechanisms of the Wallach Rearrangement . . . . S. OAE, T. FUKUMOTO and M. YAMAGAMI 1873

# *A New Method for the Determination of Boron by Spectrophotometry with Pyrocatechol Violet*

By Kazuo HIIRO

(Received December 7, 1960)

For the photometric determination of boron, most of the reagents such as oxyanthraquinones are used in concentrated sulfuric acid media, in another case using curcumin, the sample solution should be evaporated with the reagent solution under carefully controlled conditions for color development. Since these procedures are very tedious and time consuming, it would seem very useful if the color development could be substantiated simply and rapidly in aqueous media.

In previous publications it has been reported that some of the colorimetric reagents such as polyvinylalcohol[1,2], chromotropic acid[3], victoria violet[4,5] and H-resorcinol[6] can be used in aqueous media, and that some reagents are applied to indirect methods. However, many of them are not always applicable to routine work, as they are less accessible reagents, and in the case of chromotropic acid the measurements must be carried out in the ultraviolet region.

Pyrocatechol violet, a kind of sulfophthalein dye, is generally used as a metallochromic indicator for chelatometry and as photometric reagent for many metal ions such as zirconium[7,8], thorium[7], copper[10], bismuth[11], aluminum[12] and yttrium[13]. Patrovský[14] studied the detection of boron, niobium, germanium and tantalum using this reagent.

In this paper the application of the reagent to the determination of boron has been described, and the proposed method is very convenient and useful, because the procedure is carried out in an aqueous medium and the absorbance can be measured in the visible region. In this study, the absorption curves of dilute pyrocatechol violet solutions with various pH values were taken, and the existence of an isosbestic point at 494 mμ was confirmed, various facts including the effect of pH and of the reagent concentration, stability of the color and effect of temperature and of the sort of buffer solutions were examined. The interference of diverse metal ions is masked by adding ethylenediaminetetra-acetate solution as a sequestering agent. Beer's law is obeyed in the range 0.2 to 2.0 p. p. m. of boron at 494 mμ.

## Experimental

**Apparatus.** — Spectrophotometric measurements were made with a Shimadzu quartz spectrophotometer, Model QB-50, with 1 cm. glass transmission cells. A Horiba glass electrode pH meter, Model H-3 was used for all pH measurements.

**Materials.**—*Standard Boron Solutions.* — Dissolve 0.5716 g. of reagent grade boric acid in 1000 ml. of water. One milliliter of the solution corresponds to 100 μg. of boron. Dilute an aliquot of the solution with water, and prepare 10.0 p. p. m. and 5.0 p. p. m. of standard boron solutions.

*Pyrocatechol Violet Solution.* — Prepare a $2\times10^{-3}$ M aqueous solution (Dotite PV).

*Buffer Solutions.*—Prepare an ammonium chloride-ammonium hydroxide buffer solution by mixing 8 parts of 0.5 M ammonium chloride solution and 1 part of 0.5 M aqueous ammonia solution, and adjust the pH to 8.55~8.60. Veronal buffer solution is prepared as follows. To 100 ml. of mixed solution of M/7 sodium diethylbarbiturate and M/7 sodium acetate add 40 ml. of 0.85% sodium chloride solution and 25 ml. of 0.1 N hydrochloric acid, and adjust to pH 8.55~8.60.

*Ethylenediaminetetraacetate Solution.* — Dissolve disodium ethylenediaminetetraacetate (dihydrate) in water to make the concentration of $5\times10^{-2}$ M.

Other various salt solutions are prepared from analytical grade reagents.

**Measurement of Absorption Spectra of Pyrocatecholviolet.** — Twenty milliliters of $10^{-4}$ M pyrocatechol violet solutions were mixed with 5 ml. of veronal buffer solutions of various pH values and diluted to 50 ml. with water. The absorption spectra of these solutions were measured with water as reference.

**Procedure.**—Pipet the boron solution containing

1) R. F. Muraca and E. S. Jacobs, *Chemist-Analyst*, **44**, 14 (1955).
2) A. J. Monte-Bovi, J. J. Sciarra and C. Martorana, *Drug Standards*, **27**, 15 (1959); *Anal. Abstr.*, **6**, 4307 (1959).
3) D. F. Kuemmel and M. G. Mellon, *Anal. Chem.*, **29**, 378 (1957).
4) C. A. Reynolds, *U. S. Atomic Energy Comm.*, Rep. AECU-3845, 12 (1958); *Anal. Abstr.*, **6**, 2499 (1959).
5) C. A. Reynolds, *Anal. Chem.*, **31**, 1102 (1959).
6) V. A. Griso and E. N. Poluektova, *Zhur. anal. Khim.*, **13**, 434 (1958).
7) J. P. Young, J. R. French and J. C. White, *Anal. Chem.*, **30**, 422 (1958).
8) Yu. A. Cherniknov, W. F. Lukyanov and E. M. Knyazeva, *Zhur. anal. Khim.*, **14**, 207 (1959).
9) M. Svach, *Z. anal. Chem.*, **149**, 414 (1956).
10) M. Svach, ibid., **149**, 417 (1956).
11) M. Svach, ibid., **149**, 325 (1956).
12) Communication, *Anal. Chem.*, **32**, 725 (1960).
13) J. P. Young, J. C. White and R. G. Ball, ibid., **32**, 928 (1960).
14) V. Patrovský, *Chem. listy*, **51**, 968 (1957); *Anal. Abstr.*, **4**, 3593 (1957).

25 μg. or 50 μg. of boron into a 25 ml. measuring flask, add 5 ml. of $2\times10^{-3}$ M pyrocatechol violet solution and 5 ml. of buffer solution at pH 8.55~8.60, and dilute to the mark with water. Measure the absorption at 494 mμ; use a mixed solution containing 5 ml. of pyrocatechol violet and buffer in 25 ml. as reference.

In order to study the effect of diverse salts, color developments were made using 25 μg. of boron with various amounts of 4% salt solutions, and measurements were made for the solution with 50 μg. of several cations.

The effect of the temperature upon the absorbance was investigated as follows. Solutions containing 2.0 p. p. m. of boron were warmed in a water bath at a proper temperature for 15 min., and the absorbance of the solutions was measured against a reference treated similarly. For the solutions containing 1.0 p. p. m. of boron, absorbance and temperature of the warm solutions were measured at proper intervals.

## Results

**Absorption Spectra of Pyrocatechol Violet Solution.**—Fig. 1 shows the absorption curves of $4\times10^{-5}$ M pyrocatechol violet solutions at various pH values. It is found that, as the pH of the solution decreases, a maximum (450 mμ) appears, while when the pH increases absorbance at the absorption maximum (600 mμ) increases, and there is an isosbestic point at 494 mμ. Since the absorbance at the isosbestic point is not affected by the pH value of solutions, and the absorbance of reagent blank is always constant at the wavelength, the use of this isosbestic point is very advantageous for the determination of boron.

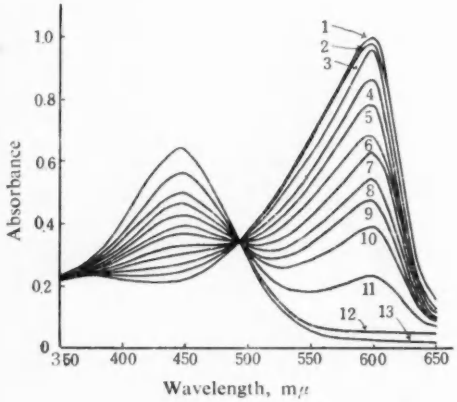



Fig. 1. Absorption spectra of pyrocatechol violet solution at various pH's.

| | | | | | |
|---|---|---|---|---|---|
| 1 | pH 9.32 | 6 | pH 8.21 | 11 | pH 7.21 |
| 2 | 8.98 | 7 | 8.10 | 12 | 5.80 |
| 3 | 8.72 | 8 | 7.95 | 13 | 4.55 |
| 4 | 8.53 | 9 | 7.79 | | |
| 5 | 8.41 | 10 | 7.63 | | |

**Effect of pH.**—As shown in Fig. 2, it is found that the maximum absorptions were obtained at pH range of 8.3~8.6.

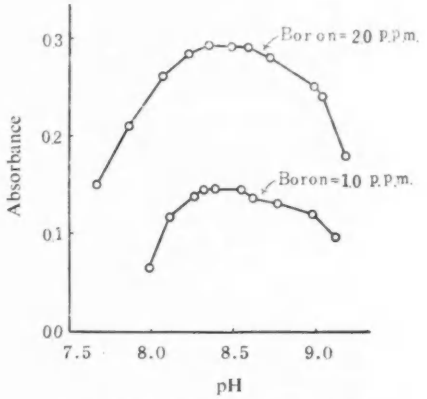



Fig. 2. Effect of pH value.
$2\times10^{-3}$ M Pyrocatechol violet soln.; 5.0 ml.,
Veronal buffer soln.; 5.0 ml.,
Measured at 494 mμ

**Absorption Spectra of Colored Boron-Pyrocatechol Violet Solution.**—Fig. 3 shows the absorption curves of the boron-pyrocatechol-violet solutions, obtained by the standard procedure. The maximum absorption is shown at 484 mμ.

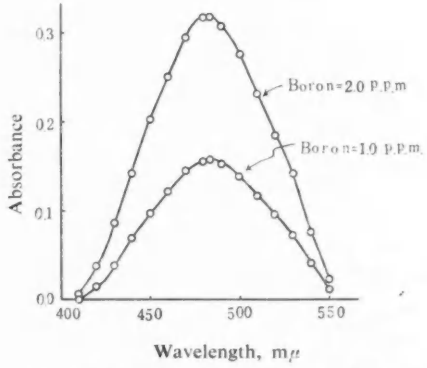
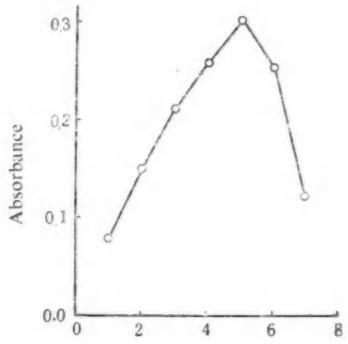



Fig. 3. Absorption spectra of colored boron-pyrocatechol violet solutions.
$2\times10^{-3}$ M Pyrocatechol violet soln.; 5.0 ml.
$NH_4Cl$-$NH_4OH$ buffer soln.; 5.0 ml.

**Reagent Concentration.**—In order to test the effect of concentration of pyrocatechol violet, a series of the absorbances was measured under various concentrations of the reagent, using the reagent blanks of the same concentration

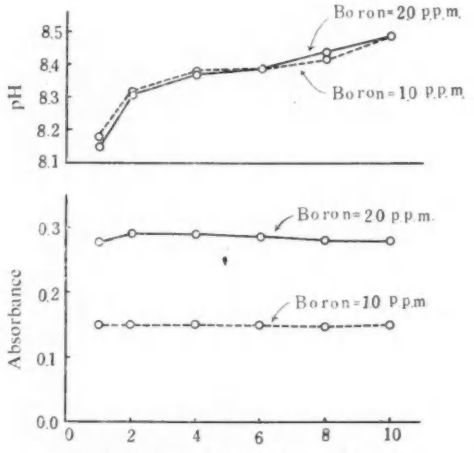
as references. As shown in Fig. 4, 5 ml. of $2\times10^{-3}$ M pyrocatechol violet solution in 25 ml. is the optimum amount.




$2\times10^{-3}$ M P. V. soln. added, ml.

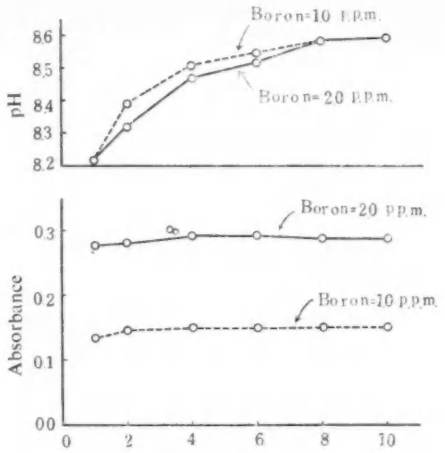
Fig. 4. Effect of pyrocatechol violet concentration.
Boron concentration; 2.0 p. p. m.
$NH_4Cl$-$NH_4OH$ buffer soln.; 5.0 ml.
Measured at 494 mμ.

**Effect of Buffer Solutions.**—The effect of buffer solution was tested with varying amounts of 0.5 M ammonium chloride-ammonia buffer solution or veronal buffer solution. At least 2 ml. of both buffer solutions are essential, as shown in Figs. 5 and 6, and 5 ml. is preferable, for the purpose of avoiding the pH change due to the addition of various salts in the following experiments.




$NH_4Cl$-$NH_4OH$ buffer soln. added, ml.

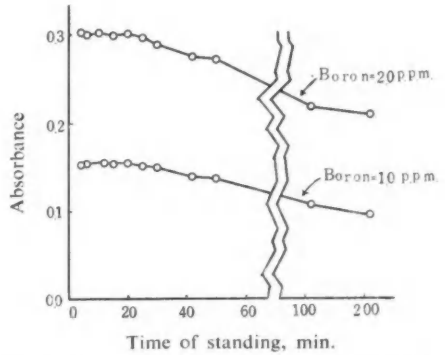
Fig. 5. Effect of buffer solution (I). In the case of ammonium chloride-ammonium hydroxide buffer solution.
$2\times10^{-3}$ M Pyrocatechol violet soln.; 5.0 ml.
Measured at 494 mμ.




Veronal buffer soln. added, ml.

Fig. 6. Effect of buffer solution (II). In the case of veronal buffer solution.
$2\times10^{-3}$ M Pyrocatechol violet soln.; 5.0 ml.
Measured at 494 mμ.

**Color Stability.**—Fig. 7 shows that the absorbance of colored solutions is constant for 20 min. Consequently the measurements should be done within 20 min. after color development.




Time of standing, min.

Fig. 7. Color stability of boron-pyrocatechol violet solutions.
$2\times10^{-3}$ M Pyrocatechol violet soln.; 5.0 ml.
Veronal buffer soln.; 5.0 ml.
Measured at 494 mμ.
Temperature; 26~27°C

**Temperature.**—It is observed that the absorbance is affected by temperature, that is, the intensity of absorbance increases as temperature is lowered, and there is an apparent linear relationship between absorbance and temperature as shown in Fig. 8. The temperature coefficients are $0.927\times10^{-2}$/°C for 2.0 p. p. m. and $0.330\times10^{-2}$/°C for 1.0 p. p. m. of boron.

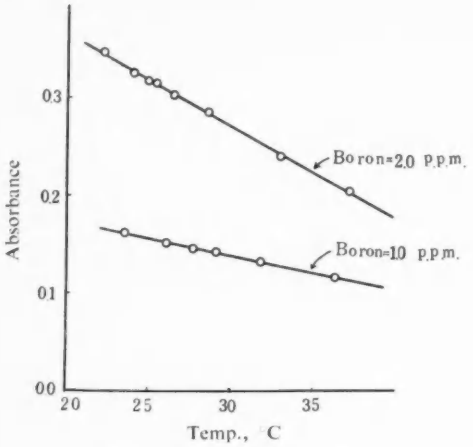



Fig. 8. Effect of temperature.

$2 \times 10^{-3}$ M Pyrocatechol violet soln.; 5.0 ml.
Veronal or $NH_4Cl$–$NH_4OH$ buffer soln.; 5.0 ml.
Measured at 494 mμ

**Stability of Pyrocatechol Violet Solution.**—The solution of pyrocatechol violet is stable for more than one month, as shown in Fig. 9.

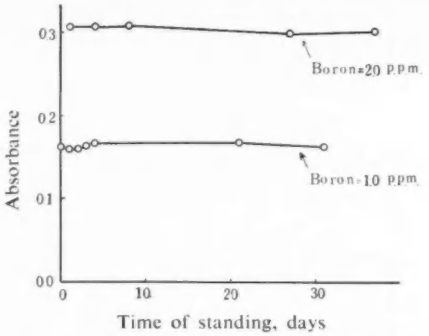



Fig. 9. Stability of pyrocatechol violet solution.

$2 \times 10^{-3}$ M Pyrocatechol violet soln.; 5.0 ml.
Veronal or $NH_4Cl$–$NH_4OH$ buffer soln.; 5.0 ml.
Measured at 494 mμ

**Diverse Salts.**—The results are presented in Table I. It was found that the presence of such salts as potassium fluoride, sodium chloride, potassium iodide, sodium sulfate, disodium hydrogenphosphate and potassium sodium tartrate do not interfere even at a concentration of 200 mg. per 25 ml. But sodium sulfite

Table I. Effect of diverse salts

| Salt | Added, mg. | | | | |
|---|---|---|---|---|---|
| | 0 | 40 | 80 | 120 | 200 |
| KF | 0.159 | 0.150 | 0.156 | 0.158 | 0.158 |
| NaCl | 0.164 | 0.163 | 0.155 | 0.151 | 0.145 |
| KI | 0.159 | 0.158 | 0.151 | 0.152 | 0.150 |
| $Na_2SO_4$ | 0.153 | 0.155 | 0.158 | 0.156 | 0.153 |
| $Na_2HPO_4 \cdot 12H_2O$ | 0.156 | 0.154 | 0.155 | 0.157 | 0.152 |
| $Na_2SO_3$ | 0.154 | 0.106 | 0.099 | 0.088 | 0.074 |
| $KNO_3$ | 0.153 | 0.171 | 0.183 | 0.181 | 0.181 |
| $KNaC_4H_4O_6 \cdot 4H_2O$ | 0.155 | 0.150 | 0.157 | 0.152 | 0.152 |
| $56Na_2O \cdot 44SiO_2$ | 0.156 | 0.156 | 0.156 | 0.159 | 0.158 |
| $NaHCO_3$ | 0.153 | 0.154 | 0.154 | 0.155 | 0.156 |

Table II. Effect of diverse metal ions

| Ion | Added, mg. | | | | |
|---|---|---|---|---|---|
| | EDTA none | | $5 \times 10^{-2}$ M EDTA 0.5 ml. added | | |
| | 0 | 50 | 100 | 200 | 500 |
| Magnesium | 0.164 | 0.125 | 0.163 | 0.165 | 0.166 |
| Zinc | 0.158 | 0.091 | 0.161 | 0.155 | 0.157 |
| Copper(II) | 0.159 | 0.095 | 0.154 | 0.152 | 0.162 |
| Aluminum | 0.156 | −0.308 | −0.009 | −0.377 | −0.705 |
| Lead | 0.152 | 0.162 | 0.154 | 0.150 | 0.153 |
| Manganase(II) | | 0.030 | 0.160 | 0.157 | 0.158 |
| Nickel | | 0.070 | 0.159 | 0.153 | 0.150 |
| Cobalt(II) | | −0.015 | 0.155 | 0.152 | 0.153 |
| Cadmium | | 0.125 | 0.151 | 0.158 | 0.155 |

and potassium nitrate interfere when 40 mg. per 25 ml. are present.

**Diverse Metal Ions.**—As shown in Table II, the following ions interfere seriously: Magnesium, zinc, copper(II), manganase(II), nickel, cobalt(II), cadmium and aluminum. Since these cations form stable chelates with ethylenediaminetetraacetate, when disodium salt of ethylenediaminetetraacetate is present in concentration of $10^{-3}$ M, they are masked effectively and do not interfer even at the concentration of 20 p. p. m. However, the interference of aluminum can not be eliminated.

**Calibration Curve.**—Measurements were made for the solutions containing various amounts of boron. Beer's law is obeyed up to 2.0 p. p. m. of boron as shown in Fig. 10. The sensitivity of this method was 0.006085/$\mu$g. and the mean error was 1.59%. Standard deviation was 0.002528 in absorbance for ten reproducible measurements for each 1.0 p. p. m. of boron.

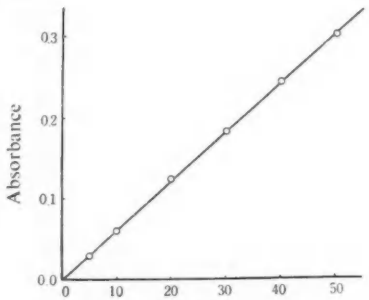



Fig. 10. Calibration curve.

$2\times10^{-3}$ M Pyrocatechol violet soln.; 5.0 ml.
$NH_4Cl$–$NH_4OH$ buffer soln.; 5.0 ml.
Measured at 494 m$\mu$
Temperature; 26~27°C.

## Discussion

The proposed new photometric method for the determination of boron by using pyrocatechol violet as a color reagent is simple in procedure as compared with the other methods.

From Fig. 1, considerations can be made as follows. Because pyrocatechol violet is a tetrabasic acid and consequently can release four protons, it may be formulated as $H_4F$, the absorption band with peak at 450 m$\mu$ can be considered as belonging exclusively to $H_3F^-$, and the peak at 600 m$\mu$ must be due to $H_2F^{2-}$ form.

As shown in Fig. 3, for the spectrophotometric measurements it is desired to choose the maximum wavelength at 482 m$\mu$, but because the absorbance of pyrocatechol violet solution is not affected by pH value at the isosbestic point 494 m$\mu$ it is preferable that the isosbestic point be chosen for the determination of boron, although photometric sensitivity is lowered slightly.

The proposed method has the feature of no preliminary separation of diverse ions, because many of them may be masked by ethylenediaminetetraacetate. This method can thus effectively be used for the determination of boron in such samples as metals, metallic oxides and alloys.

In this procedure, however, color intensity is considerably affected by temperature, so the absorption measurements must be done under constant temperature. Fortunately the effect of temperature difference will be corrected, provided that the calibration curves are made simultaneously.

Investigations for the effects of other diverse salts and metal ions and also the determination of boron for many metallic samples are now proceeding in this laboratory.

The author is indebted to Dr. Yuroku Yamamoto, Kyoto University, for his guidance and to Dr. Isao Muraki, Chief of the 5th Department of our Institute, for his useful suggestions.

*Osaka Industrial Research Institute*
*Oyodo-ku, Osaka*

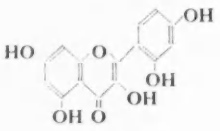
# *A New Method for the Spectrophotometric Determination of Boron with Quercetin*

By Kazuo HIIRO

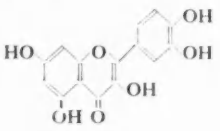
(Received January 12, 1961)

In previous publications it was reported that morin, a kind of oxyflavone, was used as a reagent for the fluorimeric and spectrophotometric determination of boron[1,2]. By an analogous consideration on the basis of the chemical constitution of the reagent, it may be said that there is a possibility of using quercetin instead of morin for the photometric determination of boron.

The formula for both compounds are:



Morin



Quercetin

In the field of photometry, quercetin was already used as a coloring reagent for germanium[3,4], zirconium[5] and molybdenum[6] etc. in previous publications. Wilson formerly reported the reactivity of boron with several kinds of flavone compounds including only a brief description on quercetin[7].

On the result of preliminary experiments the present author was confident that quercetin could be applicable to the determination of boron. In this paper, therefore, the application of the reagent to a new photometric method for boron has been described. The effects of reagent concentration, oxalic acid, and hydrogen ion concentration are examined. In addition, various conditions including temperature, duration of heating, and vessel material for evaporation of sample solution, and stability of the color, solvent of dried residue and diverse salts and the stability of the reagent solution have been investigated. It was found that the colored complex of boron-quercetin has a mole ratio of 1:1 under the proposed condition, and that Beer's law was obeyed over the range 0.00 to 0.50 p. p. m. of boron at 445 mμ.

The new photometric method for determination of boron was applied to graphite samples, and satisfactory results were obtained.

1) A. Murata and F. Yamauchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 231 (1958).
2) A. Murata and F. Yamauchi, ibid., **79**, 1454 (1958).
3) Y. Oka and S. Matsuo, ibid., **74**, 931 (1953).
4) Y. Oka and S. Matsuo, ibid., **76**, 610 (1955).
5) F. S. Grimaldi and C. E. White, *Anal. Chem.*, **25**, 1886 (1953).
6) G. Goldstein, D. L. Manning and O. Menis, ibid., **30**, 539 (1958).
7) C. W. Wilson, *J. Am. Chem. Soc.*, **61**, 2303 (1939).

## Experimental

**Apparatus.** — Spectrophotometric measurements were made with a Shimadzu quartz spectrophotometer, Model QB-50, using 1 cm. glass transmission cells. For the operation of color development a water bath of 50×35×35 cm. and an air bath of ordinary type were used.

**Materials.** — Dissolve 0.5716 g. of reagent grade boric acid in 1 l. of water to make a solution corresponding to 100.0 μg. of boron per 1.0 ml. Dilute an aliquot of the solution with water, and prepare standard solutions containing 5.0 p.p.m. and 2.0 p.p.m. of boron. Prepare a 0.2% ethanolic quercetin solution. Dissolve oxalic acid of analytical reagent grade in 95% ethanol to make a 20% solution. Prepare 1 N hydrochloric acid solution. All other salt solutions are prepared from reagents of analytical grade.

**Standard Procedure.**—Pipet an aliquot of the boron solution containing about 5.0 μg. of boron into a 100 ml. quartz beaker, add a suitable amount of water up to 2.0 ml. and add successively 1.0 ml. of 1 N hydrochloric acid, 3.0 ml. of 20% oxalic acid solution and 1.0 ml. of quercetin solution. Mix thoroughly and evaporate the contents to dryness on a water bath at 55±3°C. Subsequent to complete dryness, place the beaker in an air bath at 60~90°C, and keep it there for about 1 hr. to make sure of complete color development. After cooling to room temperature, dissolve the residue in 10 ml. of acetone and measure the absorbance at 445 mμ with acetone as reference.

To ascertain the stability of the color, read absorbance of the solution at proper intervals of time after color development. In order to study the effect of diverse salts, color developments were made using 2.0 μg. of boron in the presence of various amounts of 0.5 or 2.0% salt solutions.

Measurements of absorption spectra were made in respect to the solution obtained by the abovementioned procedure at every 5 mμ intervals of wavelength.

**Determination of Boron in Graphite Samples.**—Determination of boron in graphite samples was

made as follows[8]. Weigh powdered sample into a platinum boat, add 2.0 ml. of 3% calcium hydroxide aqueous suspension and mix well. Evaporate the graphite to dryness on a small heater, introduce the boat into a combustion tube in an electric furnace heated at 900°C and ash the sample in a current of oxygen. After cooling, remove carefully the ash into a distillation apparatus and distil off boron as methyl borate into a 100 ml. quartz beaker containing 1.4 ml. of 0.2 N sodium hydroxide solution and 9.0 ml. of water. Evaporate the contents in a quartz beaker to dryness on a water bath warmed at 40~50°C, and add 1.4 ml. of 0.2 N sulfuric acid to the dried residue and then treat as mentioned above.

## Results

**Absorption Spectra of the Complex.**—The absorption curves of colored solutions obtained by standard procedure are shown in Fig. 1. There is a maximum at 445 mμ, which suits for the spectrophotometric measurements.

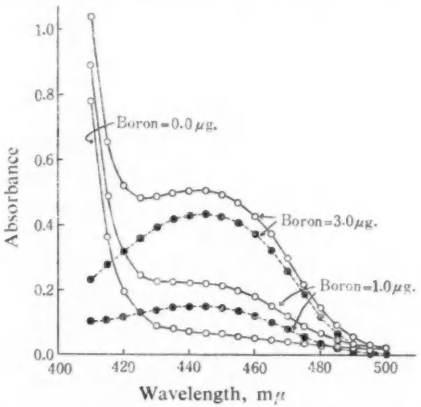



Fig. 1. Absorption spectra of colored complex of boron-quercetin.
Boron ; 3.0 μg., 1.0 μg. and 0.0 μg.
Quercetin ; 0.2% soln., 1.0 ml. (A-lot)
Oxalic acid ; 20% soln., 3.0 ml.
HCl ; 1 N soln., 1.0 ml. Water ; 3.0 ml.
—○— Obtained against acetone as reference
--●-- Obtained against blank as reference

**Reagent Concentration.**—Absorbances of a series of solutions contained 1.0 and 3.0 μg. of boron were measured in the presence of various amounts of the reagent. As shown in Fig. 2, 1.0 ml. of 0.2% quercetin solution is the optimum amount.

**Oxalic Acid Concentration.**—A test was made using 1.0 and 3.0 μg. of boron in the presence of varying amounts of 20% oxalic acid solution. The results indicate that 3.0 ml. of oxalic acid is recommended as shown in Fig. 3.

8) I. Muraki and K. Hiiro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zusshi*), **78**, 850 (1957).

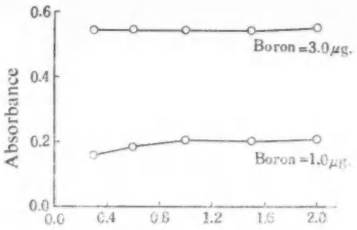



Fig. 2. Effect of quercetin added.
Boron ; 3.0 μg. and 1.0 μg.
HCl ; 1 N soln., 1.0 ml.
Oxalic acid ; 20% soln., 3.0 ml.
Water ; 3.0 ml. Quercetin ; A-lot

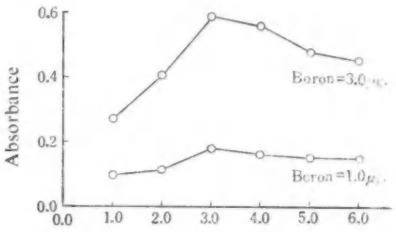



Fig. 3. Effect of oxalic acid added
Boron ; 3.0 μg. and 1.0 μg.
Quercetin ; 0.2% soln., 1.0 ml. (A-lot)
HCl ; 1 N soln., 1.0 ml. Water ; 3.0 ml.

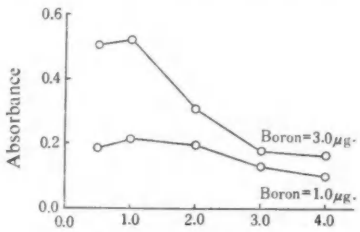



Fig. 4. Effect of hydrochloric acid added.
Boron ; 3.0 μg. and 1.0 μg.
Quercetin ; 0.2% soln., 1.0 ml. (A-lot)
Oxalic acid ; 20% soln., 3.0 ml.
Water ; 3.0 ml.

**Hydrochloric Acid Concentration.**—As shown in Fig. 4, it appears that the maximum absorption is obtained when 1.0 ml. of 1 N hydrochloric acid is used.

**Effect of Water.**—The absorbances were affected by the amount of water. As shown in Fig. 5, 3.0~4.0 ml. of water is always needed for complete color development in this procedure.

**Effect of Drying Conditions on Color Formation.** As shown in Table I, the absorbance of the resulting solution containing 2.0 μg. of boron is affected by drying conditions for color development. Most satisfactory results were obtained when evaporation was made first on a water bath at 55±3°C for 4 hr. and then in an air bath at 60 to 90°C for 1 hr.

The effect of the kind of vessel on evaporation was tested. It was desired to use a quartz beaker or a platinum basin as shown in Table II. In the cases of a glass or polyethylene beaker some interferences were observed.

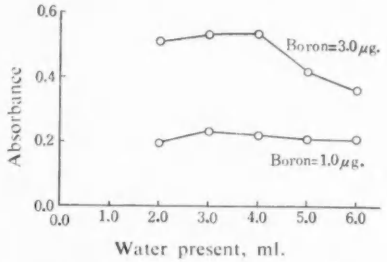



Fig. 5. Effect of water present.
Boron; 3.0 μg. and 1.0 μg.
Quercetin; 0.2% soln., 1.0 ml. (A-lot)
Oxalic acid; 20% soln., 3.0 ml.
HCl; 1 N soln., 1.0 ml.

Table I. Effect of drying conditions on color formation

Boron; 2.0 μg. Quercetin; 0.2% soln., 1.0 ml. (B-lot) Oxalic acid; 20% soln., 3.0 ml. HCl; 1 N soln., 1.0 ml. Water; 3.0 ml.

| Drying conditions | | | | Absorbance |
|---|---|---|---|---|
| On water bath (55±3°C) hr. | In air bath °C, hr. | In desiccator, hr. | In air bath °C, hr. | |
| 5.0 | | | | 0.435 |
| 6.0 | | | | 0.451 |
| 4.0 | 60, 1.0 | | | 0.466 |
| 4.0 | 60, 2.0 | | | 0.453 |
| 4.0 | 75, 0.5 | | | 0.388 |
| 4.0 | 75, 1.0 | | | 0.455 |
| 4.0 | 75, 2.0 | | | 0.466 |
| 4.0 | 90, 0.5 | | | 0.462 |
| 4.0 | 90, 1.0 | | | 0.455 |
| 4.0 | 90, 2.0 | | | 0.450 |
| 4.0 | 75, 1.0 | 40 | 75, 0.5 | 0.461 |
| 4.0 | 75, 1.0 | 40 | 75, 1.0 | 0.465 |

Table II. Effect of kinds of vessel

Boron; 2.0 μg. Quercetin; 0.2% soln., 1.0 ml.(B-lot) Oxalic acid; 20% soln., 3.0 ml. HCl; 1 N soln., 1.0 ml. Water; 3.0 ml.

| Kinds of vessel | Absorbance | Boron found μg. |
|---|---|---|
| 100 ml. Quartz beaker | 0.465 | 1.9$_8$ |
| 50 ml. Quartz beaker | 0.470 | 2.0$_0$ |
| 100 ml. Glass beaker | 0.503 | 2.1$_6$ |
| 50 ml. Glass beaker | 0.484 | 2.0$_7$ |
| Platinum basin, deep type | 0.468 | 1.9$_9$ |
| Platinum basin, shallow type | 0.470 | 2.0$_0$ |
| 100 ml. Polyethylene beaker | 0.558 | 2.4$_3$ |

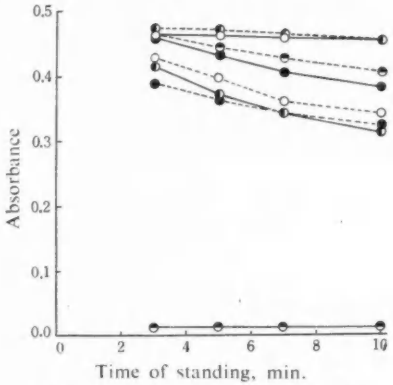



Fig. 6. Effect of kind of solvent.
Boron; 2.0 μg.
Quercetin; 0.2% soln., 1.0 ml. (B-lot)
Oxalic acid; 20% soln., 3.0 ml.
HCl; 1 N soln., 1.0 ml.
Water; 3.0 ml.
—○— Pure acetone
--○-- Acetone: Water=1:1
—●— Ethyl alcohol
—◐— Methyl isobutyl ketone
—◒— Toluene
--●-- Acetone: Water=4:1
--◐-- Methyl alcohol
--◒-- Butyl alchol
--◑-- Carbon tetrachloride

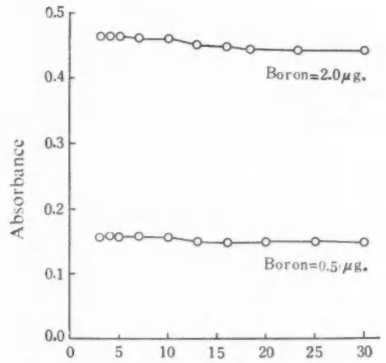



Fig. 7. Stability of the color.
Boron; 2.0 μg. and 0.5 μg.
Quercetin; 0.2% soln., 1.0 ml. (B-lot)
Oxalic acid; 20% soln., 3.0 ml.
HCl; 1 N soln., 1.0 ml.
Water; 3.0 ml.

**Effect of the Kind of Solvent on Colored Complex.**—Various kinds of solvent for extraction of boron-quercetin colored complex are tested with 2.0 μg. of boron. Fig. 6 shows that the best results are obtained in the case of pure acetone as a solvent.

**Color Stability.**—The absorbance of colored solutions is almost constant within 10 min., and then decreases slightly as shown in Fig. 7. It is thus desired to measure the absorbances within 10 min. after colored complex is dissolved with acetone.

**Stability of Quercetin Solution during Storage.**—It is found that the absorbance is increased as the duration of storage increases after preparation of the quercetin solution, and becomes constant after about 10 days as shown in Fig. 8. Hence, it is advisable to use the reagent solution after standing for about 10 days. It may be used at least 20 days after preparation.

**Effect of Diverse Salts.**—The effect of diverse ions on the spectrophotometry was examined. These salts cause interference seriously as shown in Fig. 9.

**Mole Ratio of Boron to Quercetin in Colored Complex.**—As shown in Fig. 10, maximum

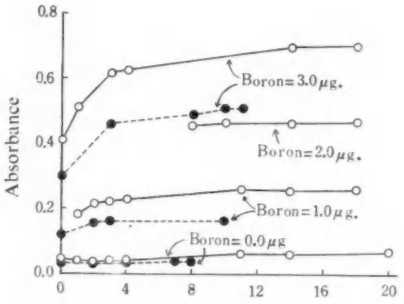



Fig. 8. Effect of duration of storage of quercetin solution.
Boron; 3.0 μg., 2.0 μg., 1.0 μg., and 0.0 μg.
Quercetin; 0.2% soln., 1.0 ml. (A- and B-lot)
Oxalic acid; 20% soln., 3.0 ml.
HCl; 1 N soln., 1.0 ml. Water; 3.0 ml.
—○— In the case of quercetin of B-lot
--◉-- In the case of quercetin of A-lot

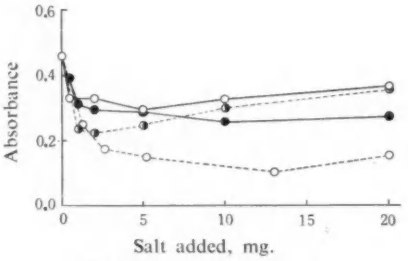



Fig. 9. Effect of diverse salts.
Boron; 2.0 μg.
Quercetin; 0.2% soln., 1.0 ml. (B-lot)
Oxalic acid; 20% soln., 3.0 ml.
HCl; 1 N soln., 1.0 ml. Water; 3.0 ml.
—○— NaCl —●— $Na_2SO_4$
--◑-- $CH_3COONa \cdot 3H_2O$
--○-- $Na_2HPO_4 \cdot 12H_2O$

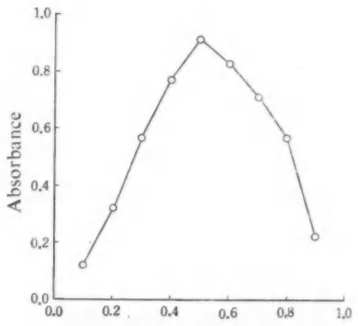



Fig. 10. Determination of ratio of boron to quercetin
Boron; $10^{-3}$ M soln., $(1.0-x)$ ml.
Quercetin; $10^{-3}$ M soln., $x$ ml. (B-lot)
Oxalic acid; 20% soln., 3.0 ml.
HCl; 1 N soln., 1.0 ml. Water; 3.0 ml.

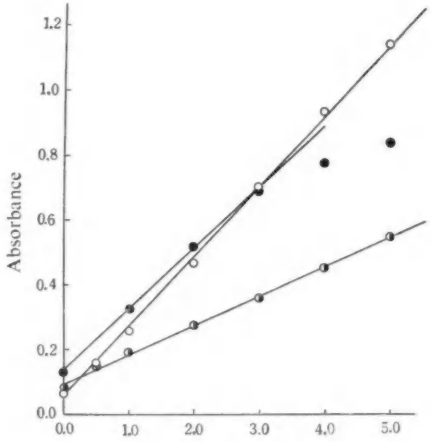



Fig. 11. Calibration curves.
Quercetin; 0.2% soln., 1.0 ml. (B-lot)
Oxalic acid; 20% soln., 3.0 ml.
HCl; 1 N soln., 1.0 ml. Water; 3.0 ml.
—○— Obtained by standard procedure
—◑— Obtained in the presence of 20 mg. of sodium sulfate
—●— Obtained after separation of boron by distillation

absorbance of the complex is obtained when the mole ratio of boron to quercetin has a value of 1 to 1[9].

**Calibration Curves.**—Measurements of absorbance were made with a number of the colored solutions containing varying amounts of boron. The results show that Beer's law is obeyed over the range 0.00 to 0.50 p. p. m. of boron as shown in Fig. 11. The sensitivity of this method, mean error and molar extinction coefficient were 0.204 $\mu$g., 4.90% and 22100 respectively. Even in the presence of 20 mg. of sodium sulfate, Beer's law is also obeyed over the range 0.00 to 0.50 p. p. m. of boron, but the sensitivity is decreased to 0.101 $\mu$g. in this case. After distillation of varying amounts of boron and evaporation of the distillate containing alkali and water to dryness, absorbances of the solutions of the dried residues were measured. As shown in Fig. 11, Beer's law is obeyed over the range 0.00 to 0.30 p. p. m. of boron.

**Determination of Boron in Graphite Samples.**—The results obtained by the above-mentioned experiments are presented in Table III.

TABLE III. RESULTS OF DETERMINATION OF BORON IN GRAPHITE SAMPLES

| Sample | Taken g. | Absorbance | Boron found $\mu$g. | Boron determined p.p.m. | Results obtained by curcumin method p.p.m. |
|---|---|---|---|---|---|
| Graphite-A | 0.5 | 0.660 | 2.8 | 5.6 | 5.53 |
| Graphite-B | 3.0 | 0.380 | 1.3 | 0.43 | 0.47 |
| Graphite-C | 2.0 | 0.450 | 1.7 | 0.85 | 0.90 |

9) W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

## Discussion

A sensitive new photometric method for the determination of boron by using quercetin as color reagent is proposed. The constitution of the boron-quercetin colored complex is considered to have the mole ratio of 1 : 1. In this procedure, if a different lot of quercetin, even though from the same maker, is used for color development, the absorbance is also varied, hence the determination of boron must be made using the calibration curve obtained by the same lot of quercetin as is used in the working operation. In this procedure, the color intensity of the solution is considerably affected by diverse salts, but the calibration curves are quite linear in the presence of a definite amount of salts. For the determination of boron in many kinds of practical samples, the proper separation of boron is desired. From the results of determination of boron in graphite samples, it was found that there is satisfactory agreement of the results obtained by the proposed method with those by the curcumin method in the limit of experimental error. This method may thus also be utilized for the determination of boron in other samples after preliminary separation of boron by distillation.

The author is indebted to Dr. Yuroku Yamamoto, Kyoto University, for his guidance and to Dr. Isao Muraki, Chief of the 5th Department of our Institute, for his useful suggestion.

*Osaka Industrial Research Institute*
*Agency of Industrial Science & Technology*
*Ministry of International Trade & Industry*
*Oyodo-ku, Osaka*

---

# *Normal Vibrations of Dimethyldimethoxysilane*

By Toshio TANAKA

(Received November 5, 1960)

The dipole moment of dimethyldimethoxysilane was previously reported to be 1.33 D at 25°C and 1.35 D at 50°C[1]. If ∠Si–O–C in this molecule was about 130° and the rotation about two Si–O bonds was free, the observed moment agreed with that calculated from bond moments. However, the ∠Si–O–C assumed there seems to be somewhat too large compared with that in tetramethoxysilane[2]. It was suggested, therefore, that the Si–O bond would perhaps rotate under some hindrance[1]. Thereafter, the Raman and the infrared spectra of dimethyldimethoxysilane were measured, and the probable form of this molecule was discussed. As the result,

1) A. kotera, K. Matsumura, H. Nomura, Y. Nakano and U. Maeda, presented at the Symposium on Organosilicon Compounds, Osaka, October, 1956, and private communication.

2) M. Yokoi, This Bulletin, **30**, 106 (1957).

it was concluded that this molecule would be *GG* form in the solid state* and have no rotational isomers[3].

This paper reports the calculation of the fundamental frequencies of this molecule and their normal mode of skeletal vibrations, under the assumption that this molecule belongs to the point group $C_{2v}$. In the calculation, a methyl group was regarded as a point mass. The normal coordinate treatment was carried out by the Wilson *FG* matrix method[4] with a Urey-Bradley potential function. No calculation of the normal vibration for $Y_2M(XZ)_2$ type molecules has been reported as far as the author knows.

## Normal Coordinate Treatment

The normal coordinate treatment has been carried out for parameters which are shown in Fig. 1. The symmetry of the molecule was assumed as $C_{2v}$. The interplanar angle for a Si–O–C plane and a C–Si–O plane including the same Si–O bond were also assumed to have an interplanar angle of $+60°$ or $-60°$.

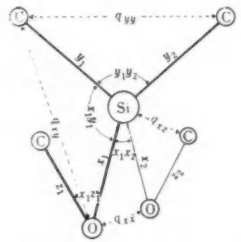



Fig. 1. Internal coordinates of the skeletal of dimethyldimethoxysilane.

According to the group theory, this molecule has fifteen skeletal vibrations, six of $a_1$, two of $a_2$, four of $b_1$ and three of $b_2$ species. Each one of the skeletal vibrations of $a_2$ and $b_2$ species is the torsional oscillation of a (Si–)$OCH_3$ group*. All vibrations of the $a_1$, $b_1$ and $b_2$ species are active both in infrared and Raman spectra, and those of the $a_2$ species are Raman active but infrared inactive.

From the internal coordinates indicated in Fig. 1, the following orthonormal symmetry coordinates have been found:

for the $a_1$ vibrations,

$$R_1 = \Delta(z_1+z_2)/\sqrt{2}$$
$$R_2 = \Delta(x_1+x_2)/\sqrt{2}$$
$$R_3 = \Delta(y_1+y_2)/\sqrt{2}$$
$$R_4 = \Delta(x_1z_1+x_2z_2)/\sqrt{2}$$
$$R_5 = \Delta(x_1x_2-y_1y_2)/\sqrt{2}$$
$$R_6 = \Delta(2x_1x_2+2y_1y_2-x_1y_1-x_1y_2-x_2y_1-x_2y_2)/\sqrt{12}$$

for the $a_2$ vibration,

$$R_7 = \Delta(x_1y_1-x_1y_2-x_2y_1+x_2y_2)/2$$

for the $b_1$ vibrations,

$$R_9 = \Delta(z_1-z_2)/\sqrt{2}$$
$$R_{10} = \Delta(x_1-x_2)/\sqrt{2}$$
$$R_{11} = \Delta(x_1z_1-x_2z_2)/\sqrt{2}$$
$$R_{12} = \Delta(x_1y_1+x_1y_2-x_2y_1-x_2y_2)/2$$

and for the $b_2$ vibrations,

$$R_{13} = \Delta(y_1-y_2)/\sqrt{2}$$
$$R_{14} = \Delta(x_1y_1-x_1y_2+x_2y_1-x_2y_2)/2$$

The numbering of these symmetry coordinates corresponds to the numbering of the fundamentals in Table I.

From the coefficients of the symmetry coordinates and the potential constants in a Urey-Bradley force field[5], the $F$ matrix elements are obtained as follows:

for the $a_1$ vibrations,

$$F_{11} = K_z + s_{zx}{}^2F_{xz} + t_{zx}{}^2F_{xz}'$$
$$F_{12} = s_{xz}s_{zx}F_{xz} - t_{xz}t_{zx}F_{xz}'$$
$$F_{14} = (s_{zx}t_{xz}F_{xz} + s_{xz}t_{zx}F_{xz}')x$$
$$F_{22} = K_x + 2s_{xx}{}^2F_{xx} + 2s_{xy}{}^2F_{xy} + s_{xz}{}^2F_{xz} + 2t_{xy}{}^2F_{xy}' + t_{xz}{}^2F_{xz}'$$
$$F_{23} = 2(s_{xy}s_{yx}F_{xy} - t_{xy}t_{yx}F_{xy}')$$
$$F_{24} = (s_{xz}t_{zx}F_{xz} + s_{zx}t_{xz}F_{xz}')z$$
$$F_{25} = s_{xx}t_{xx}(F_{xx}+F_{xx}')x$$
$$F_{26} = \sqrt{2/3}\{s_{xx}t_{xx}(F_{xx}+F_{xx}')x - (s_{xy}t_{yx}F_{xy} + s_{yx}t_{xy}F_{xy}')y\}$$
$$F_{33} = K_y + 2s_{yy}{}^2F_{yy} + 2s_{yx}{}^2F_{xy} + 2t_{yx}{}^2F_{xy}'$$
$$F_{35} = -s_{yy}t_{yy}(F_{yy}+F_{yy}')y$$
$$F_{36} = \sqrt{2/3}\{s_{yy}t_{yy}(F_{yy}+F_{yy}')y - (s_{yx}t_{xy}F_{xy} + s_{xy}t_{yx}F_{xy}')x\}$$
$$F_{44} = (H_{xz} + t_{xz}t_{zx}F_{xz} - s_{xz}s_{zx}F_{xz}')xz$$
$$F_{55} = \{(H_{xx} + t_{xx}{}^2F_{xx} - s_{xx}{}^2F_{xx}')x^2 + (H_{yy} + t_{yy}{}^2F_{yy} - s_{yy}{}^2F_{yy}')y^2\}/2 + 3\kappa/\sqrt{8}$$
$$F_{56} = \{(H_{xx} + t_{xx}{}^2F_{xx} - s_{xx}{}^2F_{xx}')x^2 - (H_{yy} + t_{yy}{}^2F_{yy} - s_{yy}{}^2F_{yy}')y^2\}/\sqrt{6}$$

* In the liquid state, the two Si–O bonds would rotate slowly centering in the *GG* form[3].

3) M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **79**, 436 (1958).

4) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939).

* Represents the methoxyl group attached to silicon atom.

5) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

$$F_{66}=\{(H_{xx}+t_{xx}{}^2F_{xx}-s_{xx}{}^2F_{xx}')x^2+(H_{xy}+t_{xy}t_{yx}F_{xy}-s_{xy}s_{yx}F_{xy}')xy+(H_{yy}+t_{yy}{}^2F_{yy}-s_{yy}{}^2F_{yy}')y^2\}/3+\kappa/\sqrt{8}$$

$$F_{13}=F_{15}=F_{16}=F_{34}=F_{45}=F_{46}=0$$

for the $a_2$ vibration,

$$F_{77}=(H_{xy}+t_{xy}t_{yx}F_{xy}-s_{xy}s_{yx}F_{ny}')xy-\kappa/\sqrt{8}$$

for the $b_1$ vibrations,

$$F_{99}=K_z+s_{zz}{}^2F_{zz}+t_{zz}{}^2F_{zz}'$$

$$F_{910}=s_{zz}s_{zx}F_{zz}-t_{zz}t_{zx}F_{zz}'$$

$$F_{911}=(s_{zz}t_{zz}F_{zz}+s_{zz}t_{zx}F_{zz}')x$$

$$F_{1010}=K_x+2s_{xy}{}^2F_{xy}+s_{xz}{}^2F_{zz}+2t_{xx}{}^2F_{xx}'+2t_{xy}{}^2F_{xy}'+t_{xz}{}^2F_{zz}'$$

$$F_{1011}=(s_{xz}t_{zx}F_{xz}+s_{zx}t_{zz}E_{zz}')z$$

$$F_{1012}=\sqrt{2}\,(s_{xy}t_{yx}F_{xy}+s_{yx}t_{xy}F_{xy}')y$$

$$F_{1111}=(H_{xz}+t_{xz}t_{zx}F_{zz}-s_{zz}s_{zx}F_{zz}')xz$$

$$F_{1212}=(H_{xy}+t_{xy}t_{yx}F_{xy}-s_{xy}s_{yx}F_{xy}')xy+3\kappa/\sqrt{8}$$

$$F_{912}=F_{1112}=0$$

and for the $b_2$ vibrations,

$$F_{1313}=K_y+2s_{yx}{}^2F_{xy}+2t_{yx}{}^2F_{xy}'+2t_{yy}{}^2F_{yy}'$$

$$F_{1314}=\sqrt{2}\,(s_{yx}t_{xy}F_{xy}+s_{xy}t_{yx}F_{xy}')x$$

$$F_{1414}=(H_{xy}+t_{xy}t_{yx}F_{xy}-s_{xy}s_{yx}F_{xy}')xy+3\kappa/\sqrt{8}$$

where the following abbreviations have been adopted:

| | |
|---|---|
| $s_{xx}=4x/3q_{xx}$ | $t_{xx}=\sqrt{8}\,x/3q_{xx}$ |
| $s_{yy}=4y/3q_{yy}$ | $t_{yy}=\sqrt{8}\,y/3q_{yy}$ |
| $s_{xy}=(3x+y)/3q_{xy}$ | $t_{xy}=\sqrt{8}\,y/3q_{xy}$ |
| $s_{yx}=(3y+x)/3q_{xy}$ | $t_{yx}=\sqrt{8}\,x/3q_{xy}$ |
| $s_{xz}=(x-z\cos\theta)/q_{xz}$ | $t_{xz}=z\sin\theta/q_{xz}$ |
| $s_{zx}=(z-x\cos\theta)/q_{xz}$ | $t_{zx}=x\sin\theta/q_{xz}$ |

and the symbols used for the equilibrium values of the interatomic distances and of the interbond angles are $x$=Si—O, $y$=Si—C, $z$=O—C, $q_{xx}$=O···O, $q_{yy}$=C···(Si)···C, $q_{xy}$=O···C, $q_{xz}$=Si···C and $\theta=\angle$SiOC.

The $G$ matrix elements are obtained by the use of the table of Decius[6] and the method of Crawford[7]. Using the notations $\rho_x$, $\rho_y$ and $\rho_z$ for the reciprocals of Si—O, Si—C and O—C bond lengths, and $\mu_{Si}$, $\mu_O$ and $\mu_C$ for the reciprocals of the masses of silicon and oxygen atoms and methyl group, respectively, the following $G$ matrix elements have been obtained:

for the $a_1$ vibrations,

$$G_{11}=\mu_O+\mu_C$$

$$G_{12}=\mu_O\cos\theta$$

$$G_{14}=-\rho_x\mu_O\sin\theta$$

$$G_{15}=-\rho_x\mu_O\sin\theta$$

$$G_{16}=-\sqrt{3}\,\rho_x\mu_O\sin\theta/\sqrt{2}$$

$$G_{22}=2\mu_{Si}/3+\mu_O$$

$$G_{23}=-2\mu_{Si}/3$$

$$G_{24}=-\sqrt{8}\,\rho_x\mu_{Si}/3$$

$$G_{25}=-\sqrt{8}\,(\rho_x+\rho_y)\mu_{Si}/3$$

$$G_{26}=-2(\rho_x-\rho_y)\mu_{Si}/\sqrt{3}$$

$$G_{33}=2\mu_{Si}/3+\mu_C$$

$$G_{34}=\sqrt{8}\,\rho_x\mu_{Si}/3$$

$$G_{35}=\sqrt{8}\,(\rho_x+\rho_y)\mu_{Si}/3$$

$$G_{36}=2(\rho_x-\rho_y)\mu_{Si}/\sqrt{3}$$

$$G_{14}=4\rho_x{}^2\mu_{Si}/3+\rho_z{}^2\mu_C+(\rho_x{}^2+\rho_z{}^2-2\rho_x\rho_z\cos\theta)\mu_O$$

$$G_{45}=4\rho_x(\rho_x+\rho_y)\mu_{Si}/3+\rho_x(\rho_x-\rho_z\cos\theta)\mu_O$$

$$G_{46}=\sqrt{8}\,\rho_x(\rho_x-\rho_y)\mu_{Si}/\sqrt{3}+\sqrt{3}\,\rho_x(\rho_x-\rho_z\cos\theta)\mu_O/\sqrt{2}$$

$$G_{55}=4(\rho_x+\rho_y)^2\mu_{Si}/3+\rho_x{}^2\mu_O+\rho_y{}^2\mu_C$$

$$G_{56}=\sqrt{8}\,(\rho_x{}^2-\rho_y{}^2)\mu_{Si}/\sqrt{3}+\sqrt{3}\,(\rho_x{}^2\mu_O-\rho_y{}^2\mu_C)/\sqrt{2}$$

$$G_{66}=2(\rho_x-\rho_y)^2\mu_{Si}+3(\rho_x{}^2\mu_O+\rho_y{}^2\mu_C)/2$$

$$G_{13}=0$$

for the $a_2$ vibration,

$$G_{77}=3(\rho_x{}^2\mu_O+\rho_y{}^2\mu_C)/2$$

for the $b_1$ vibrations,

$$G_{99}=\mu_O+\mu_C$$

$$G_{910}=\mu_O\cos\theta$$

$$G_{911}=-\rho_x\mu_O\sin\theta$$

$$G_{912}=\rho_x\mu_O\sin\theta/\sqrt{2}$$

$$G_{1010}=4\mu_{Si}/3+\mu_O$$

$$G_{1011}=\sqrt{8}\,\rho_x\mu_{Si}/3-\rho_x\mu_O\sin\theta$$

$$G_{1012}=-2(\rho_x+3\rho_y)\mu_{Si}/3$$

$$G_{1111}=\rho_z{}^2(\mu_O+\mu_C)+\rho_x{}^2(2\mu_{Si}/3+\mu_O)-2\rho_x\rho_y\mu_O\cos\theta$$

$$G_{1112}=-\sqrt{2}\,\rho_x(\rho_x+3\rho_y)\mu_{Si}/3-\rho_x(\rho_x-\rho_z\cos\theta)\mu_O/\sqrt{2}$$

$$G_{1212}=(\rho_x{}^2\mu_O+3\rho_y{}^2\mu_O)/2+(\rho_x+3\rho_y)^2\mu_{Si}/3$$

for the $b_2$ vibrations,

$$G_{1313}=4\mu_{Si}/3+\mu_C$$

6) J. C. Decius, ibid., **16**, 1025 (1948).
7) B. Crawford, ibid., **21**, 1108 (1953).

$G_{1314} = -2(\rho_x + \rho_y/3)\mu_{Si}$

$G_{1414} = (3\rho_x{}^2\mu_O + \rho_y{}^2\mu_C)/2 + (3\rho_x + \rho_y)^2\mu_{Si}/3$

The molecular and potential constants used in the calculation are listed in Table I. These values are the same as those in the preceding paper[8] except $H_{yy}$, $F_{yy}$ and $\kappa$. The potential constants of $H(CH_3\text{–}Si\text{–}CH_3)$ and $F(CH_3\cdots CH_3)$ in tetramethylsilane[9] have been adopted for the $H_{yy}$ and $F_{yy}$ in the molecule under consideration. The $\kappa$ in this molecule has been assumed to be the mean between that in tetramethylsilane[9] and that in tetramethoxysilane[10]. The values of $F'$ have been assumed to be equal to $-F/10$ in the usual way.

TABLE I. MOLECULAR AND POTENTIAL CONSTANTS OF DIMETHYLDIMETHOXYSILANE

| Bond distance and angle | Potential constant | |
|---|---|---|
| | Type | md./Å |
| $x$=Si—O | $K_x$(Si—O) | 3.25 |
| =1.64 Å[a] | $K_y$(Si—$CH_3$) | 3.03 |
| $y$=Si—C | $K_z$(O—$CH_3$) | 4.88 |
| =1.888 Å[b] | $H_{xx}$(O—Si—O) | 0.13 |
| $z$=O—C | $H_{xy}$(O—Si—$CH_3$) | 0.12 |
| =1.42 Å[a] | $H_{yy}$($CH_3$—Si—$CH_3$) | 0.11 |
| ∠OSiC | $H_{xz}$(Si—O—$CH_3$) | 0.22 |
| =∠OSiC | $F_{xx}$(O···O) | 0.13 |
| =∠CSiC | $F_{xy}$(O···$CH_3$) | 0.08 |
| =109°28 | $F_{yy}$($CH_3$···$CH_3$) | 0.034 |
| =∠SiOC | $F_{xz}$(Si···$CH_3$) | 0.21 |
| =113°[a] | $\kappa$ | 0.185 Å$^2$ |

a) Values in $Si(OCH_3)_4$; M. Yokoi, This Bulletin, **30**, 100 (1957).
b) Value in $Si(CH_3)_4$; W. F. Sheehan, Jr. and V. Schomaker, *J. Am. Chem. Soc.*, **74**, 3956 (1952).

### Assignments of the Observed Frequencies

From the $F$ and $G$ matrix elements given above, the fundamental frequencies have been calculated by the use of the molecular and the potential constants listed in Table I, and the results are shown in Table II, together with the observed wave numbers[a] of the Raman and the infrared bands in the region of the skeletal vibrations. The skeletal vibrations have been assigned by the calculation of the potential energy distribution in the symmetry coordinates.

In the present calculation, the wave number of the Si–O symmetrical stretching vibration($a_1$) is higher than that of the Si–O nonsymmetrical stretching vibration($b_1$). Nevertheless, the observed frequencies near 690 and 735 cm$^{-1}$ have been assigned as $\nu_2(a_1)$ and $\nu_{10}(b_1)$, respectively (Table II), considering the intensities of Raman and infrared bands.

As is shown in Table II, the calculated values of $\nu_2$ and $\nu_{10}$ are considerably higher than the observed ones, respectively. In order to get a better agreement between the calculated wave number and the observed, it is necessary

TABLE II. RAMAN AND INFRARED DATA, CALCULATED WAVE NUMBERS AND THE ASSIGNMENT FOR DIMETHYLDIMETHOXYSILANE

| $\nu$. Obs. | | $\nu$. Calcd. | Assignment | Mode of vibration |
|---|---|---|---|---|
| Raman[a] | Infrared[a] | | | |
| 98 (1b) | | 136 | $\nu_6$ ($a_1$) | $Si(CH_3)_2$+$SiO_2$ sym. def. |
| | | 190 | $\nu_{12}$ ($b_1$) | $SiO_2$ rocking |
| 218 (4) | | 208 | $\nu_7$ ($a_2$) | $Si(CH_3)_2$ twisting |
| | | 238 | $\nu_5$ ($a_1$) | $Si(CH_3)_2$+$SiO_2$ nonsym. def. |
| 260 (2) | | 288 | $\nu_4$ ($a_1$) | SiOC sym. def. |
| 355 (0) | | 302 | $\nu_{14}$ ($b_2$) | $Si(CH_3)_2$ rocking |
| 380 (4bb) | | 400 | $\nu_{11}$ ($b_1$) | SiOC nonsym. def. |
| 618 (106) | 613 (w) | 618 | $\nu_3$ ($a_1$) | Si—C sym. str. |
| | 673 (w) | | | |
| 691 (3) | 690 (w) | 813 | $\nu_2$ ($a_1$) | Si—O sym. str. |
| 736 (2) | 730 (s) | 779 | $\nu_{10}$ ($b_1$) | Si—O nonsym. str. |
| 804 (5) | 797 (s) | 791 | $\nu_{13}$ ($b_2$) | Si—C nonsym. str. |
| 845 (1) | 849 (vs) | | } | (Si—)$CH_3$ rocking |
| 865 (2) | | | } | |
| 995 (1) | 998 (vw) | | | |
| 1080 (2) | 1073 (vs) | 1069 | $\nu_9$ ($b_1$) | C—O nonsym. str. |
| | 1088 (sh) | 1071 | $\nu_1$ ($a_1$) | C—O sym. str. |

a) Values in the liquid state

8) T. Tanaka, This Bulletin, **33**, 446 (1960).
9) T. Shimanouchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 266 (1953).
10) H. Murata, ibid., **77**, 893 (1956).

Table III. The $L$ matrices of the skeletal normal vibrations of dimethyldimethoxysilane

$a_1$ vibrations

| | $Q_1$ | $Q_2$ | $Q_3$ | $Q_4$ | $Q_5$ | $Q_6$ |
|---|---|---|---|---|---|---|
| $R_1$ (C—O sym. str.) | 0.36 | −0.03 | 0.02 | −0.02 | 0.00 | 0.01 |
| $R_2$ (Si—O sym. str.) | −0.10 | −0.23 | 0.14 | −0.04 | 0.00 | 0.00 |
| $R_3$ (Si—C sym. str.) | 0.01 | 0.22 | 0.20 | 0.01 | 0.01 | 0.00 |
| $R_4$ (SiOC sym. def.) | −0.07 | 0.23 | −0.15 | −0.18 | 0.10 | 0.06 |
| $R_5$ ($Si(CH_3)_2$+$SiO_2$ nonsym. def.) | −0.08 | 0.21 | −0.02 | −0.16 | −0.16 | −0.04 |
| $R_6$ ($Si(CH_3)_2$+$SiO_2$ sym. def.) | −0.12 | 0.05 | −0.04 | −0.06 | 0.15 | −0.14 |

$b_1$ vibrations

| | $Q_9$ | $Q_{10}$ | $Q_{11}$ | $Q_{12}$ |
|---|---|---|---|---|
| $R_9$ (C—O nonsym. str.) | 0.35 | −0.07 | 0.01 | 0.00 |
| $R_{10}$ (Si—O nonsym. str.) | −0.13 | −0.30 | −0.01 | −0.01 |
| $R_{11}$ (SiOC nonsym. def.) | −0.08 | 0.09 | 0.30 | −0.10 |
| $R_{12}$ ($SiO_2$ rocking) | 0.10 | 0.14 | −0.21 | −0.14 |

$b_2$ vibrations

| | $Q_{13}$ | $Q_{14}$ |
|---|---|---|
| $R_{13}$ (Si—C nonsym. str.) | −0.33 | −0.03 |
| $R_{14}$ ($Si(CH_3)_2$ rocking) | 0.18 | −0.28 |

Table IV. Potential energy distribution $F_{ii}L_{ia}^2/\lambda_a$ for the normal vibration of skeletal in dimethyldimethoxysilane

$a_1$ vibrations

| | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_6$ |
|---|---|---|---|---|---|---|
| $R_1$ (C—O sym. str.) | 0.94 | 0.01 | 0.01 | 0.05 | 0.00 | 0.01 |
| $R_2$ (Si—O sym. str.) | 0.05 | 0.50 | 0.33 | 0.11 | 0.00 | 0.00 |
| $R_3$ (Si—C sym. str.) | 0.00 | 0.39 | 0.59 | 0.01 | 0.01 | 0.00 |
| $R_4$ (SiOC sym. def.) | 0.01 | 0.09 | 0.07 | 0.42 | 0.20 | 0.22 |
| $R_5$ ($Si(CH_3)_2$+$SiO_2$ nonsym. def.) | 0.01 | 0.07 | 0.00 | 0.32 | 0.53 | 0.08 |
| $R_6$ ($Si(CH_3)_2$+$SiO_2$ sym. def.) | 0.01 | 0.00 | 0.00 | 0.03 | 0.26 | 0.69 |

$b_1$ vibrations

| | $\nu_9$ | $\nu_{10}$ | $\nu_{11}$ | $\nu_{12}$ |
|---|---|---|---|---|
| $R_9$ (C—O nonsym. str.) | 0.91 | 0.08 | 0.01 | 0.00 |
| $R_{10}$ (Si—O nonsym. str.) | 0.09 | 0.89 | 0.01 | 0.02 |
| $R_{11}$ (SiOC nonsym. def.) | 0.00 | 0.01 | 0.66 | 0.33 |
| $R_{12}$ ($SiO_2$ rocking) | 0.01 | 0.03 | 0.32 | 0.64 |

$b_2$ vibrations

| | $\nu_{13}$ | $\nu_{14}$ |
|---|---|---|
| $R_{13}$ (Si—C nonsym. str.) | 0.96 | 0.04 |
| $R_{14}$ ($Si(CH_3)_2$ rocking) | 0.06 | 0.95 |

to adopt a lower value of $K_x$(Si—O), than the 3.25 md./Å of methyltrimethoxysilane[8]. Accordingly, it seems that the value of $K_x$(Si—O) in dimethyldimethoxysilane is rather lower than that in methyltrimethoxysilane. This may correspond to the tendency for the bond energy of Si–O bond which decreases as the number of oxygen atoms attached to silicon decreases; $-E_{Si-O}$ in $SiO_4$ unit $>$ $-E_{Si-O}$ in $CSiO_3$ unit $>$ $-E_{Si-O}$ in $C_2SiO_2$ unit, as reported by the present author[11].

The $L$ matrices and the distribution of potential energy in symmetry coordinates have been calculated for the skeletal normal modes; the results are shown in Tables III and IV, respectively. As shown in Table IV, some of the symmetry coordinates of totally symmetric species are related to several normal modes to a considerable extent; the $R_2$ and $R_3$ coordinates to both modes of $\nu_2$ and $\nu_3$, and the $R_4$ and $R_5$ coordinates to a mode of $\nu_4$.

The author wishes to express his sincere thanks to Professor Takeo Watase of this University, Professor Hiroshi Azumi of Tohoku University and Dr. Hiroshi Murata of Hiroshima University for much valuable discussion.

*Department of Applied Chemistry*
*Faculty of Engineering*
*Osaka University*
*Miyakojima-ku, Osaka*

11) T. Tanaka, *J. Inorg. Nucl. Chem.*, **13**, 225 (1961).

# *Thermodynamic Studies on Cobalt Complexes. VIII. Some Information about Diaquotetramminecobalt(III) Complexes and Thermal Dissociation of the Corresponding Chloride**

By Motoshichi MORI, Ryokichi TSUCHIYA, Shuji TAKEMURA and Eisei MATSUDA

(Received December 19, 1960)

Although there have been a few reports[1,2] on the visible and ultraviolet absorption spectra of diaquotetramminecobalt(III) complexes, none can be found on the infrared absorption spectra of cobalt(III) diaquo-complexes except in the cases of $[Co(NH_3)_2(OH_2)_2Cl_2]Cl$ and $[Co\,en(OH_2)_2Cl_2]Cl$[3] containing chloride ions as the ligand. The investigation of diaquotetramminecobalt(III) complexes by X-ray diffraction method has never been reported. In the present study the infrared absorption and the X-ray diffraction of diaquotetramminecobalt(III) and aquopentamminecobalt(III) complexes were measured. From these some information about their crystal structures was brought out. Since little has been reported concerning the thermochemical properties of cobalt(III) diaquo-complexes, some of them will be described, with special reference to the thermal dissociation of the diaquotetramminecobalt(III) chloride.

## Experimental

Diaquotetramminecobalt(III) chloride, sulfate and perchlorate were prepared[4] by the aquation of carbonatotetramminecobalt(III) nitrate with hydrochloric, sulfuric and perchloric acids respectively. Their visible and ultraviolet absorption spectra were measured with a Hitachi EPU-2 type spectrophotometer. The infrared absorption of diaquotetramminecobalt(III) and aquopentamminecobalt(III) perchlorates were measured by the Nujol mull method with an Ōyō Kōgaku Kenkyūsho DS-201 infrared spectrophotometer, and the X-ray diffraction, with a Rigaku Denki X-ray diffractometer. The results obtained were compared with those of hexamminecobalt(III) perchlorate.

The thermal analysis was carried out for diaquotetramminecobalt(III) chloride, sulfate and perchlorate with a Shimadzu thermobalance. The thermal dissociation pressure of diaquotetramminecobalt(III) chloride was measured in vacuo with a mercury manometer.

## Results and Discussion

**Thermal Analyses of Diaquotetramminecobalt(III) Chloride, Sulfate and Perchlorate.**— In order to verify the fact that the complexes obtained were actually the desired ones, chemical analyses, determinations of coagulation values and thermal analyses were made with them. The weight losses of the complexes upon heating are plotted against the temperature in Fig. 1. It is presumed that the chloride and sulfate decompose according to the following schemes:

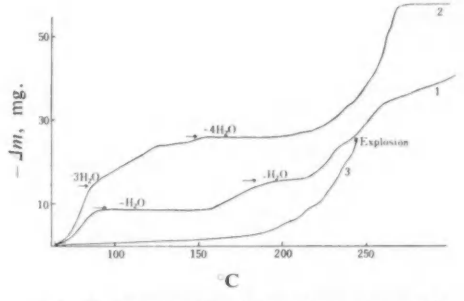



Fig. 1. The relationships between the weight loss and the temperature upon heating diaquotetramminecobalt(III) chloride (1), sulfate hydrate (2) and perchlorate (3). Both the weights of the chloride and of the perchlorate used are 0.2 g. respectively and that of the sulfate hydrate is 0.1 g. The expressions of $-nH_2O$ show the steps of dehydration of $n$ g molecule of water from oneg ram molecule of those complexes.

$$[Co(NH_3)_4(OH_2)_2]Cl_3 \xrightarrow[70\sim90°C]{-H_2O} [Co(NH_3)_4(OH_2)Cl]Cl_2 \xrightarrow[150\sim170°C]{-H_2O} cis\text{-}[Co(NH_3)_4Cl_2]Cl \xrightarrow[200\sim234°C]{} CoCl_2$$

* Read at the Symposium on Coordination Compounds of the Chemical Society of Japan, Sendai, September, 1960.

1) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 312 (1956).

2) A. Kiss and D. Czeglédy, *Z. anorg. u. allgem. Chem.*, **235**, 407 (1938).

3) E. Kyuno, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 724 (1959).

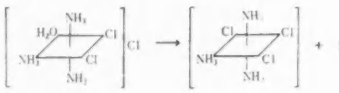
4) S. M. Jörgensen, *Z. anorg. Chem.*, **2**, 296 (1892).

$$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3 \cdot 3H_2O \xrightarrow[80°C]{-3H_2O},$$

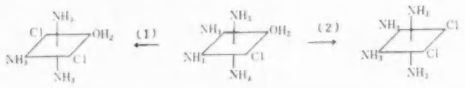
$$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3 \xrightarrow[90\sim150°C]{-4H_2O}, [Co(NH_3)_4SO_4]_2SO_4 \xrightarrow{240\sim260°C}, 2CoSO_4 + (NH_4)_2SO_4$$

The perchlorate begins to decompose gently at about 190°C and explodes at 243°C. The decomposition of the perchlorate does not take place in a stepwise manner as does the chloride and sulfate.

*trans*-Aquodichlorotriamminecobalt(III) chloride, $[Co(NH_3)_3(OH_2)Cl^{(1)}_{2(6)}]Cl$, does not decompose at 100°C, whereas even at this temperature the corresponding *cis*-chloride changes to trichlorotriamminecobalt(III) complex releasing water as shown below:



There has been a report[5] that this phenomenon might be explained by the so-called trans-effect[6]. If the trans-effect is to be applied to the decomposition of aquochlorotetramminecobalt(III) chloride, the product must be *trans*-aquodichlorotriamminecobalt(III) chloride, $[Co(NH_3)_3(OH_2)Cl^{(1)}_{2(6)}]Cl$. But the product actually obtained in our experiment is *cis*-dichlorotetramminecobalt(III) chloride, $[Co(NH_3)_4Cl^{(1)}_{2(2)}]Cl$; i. e. process 1 did not occur, but process 2 did take place:



This shows that the trans-effect can not be applied to this process. A better explanation may be that *cis*-dichlorotetramminecobalt(III) chloride is more stable than the corresponding trans-chloride in the same way as that *cis*-dinitrotetramminecobalt(III) chloride is thermodynamically more stable than the corresponding *trans*-chloride[7].

**Visible and Ultraviolet Absorption Spectra of Diaquotetramminecobalt(III) Complexes.**—The visible and ultraviolet absorption spectra of diaquotetramminecobalt(III) complex which have already been reported by Tsuchida and his co-worker[1] and Kiss and his co-worker[8] are not in agreement with each other. That is, the maxima of both the first and second absorption bands of the complex reported by the former workers* are remarkably lower than those by the latter. The absorption of the complex measured by us are given in Fig. 2. The maxima of the first and second absorption bands of the complex are found at $\nu_1 = 59.0 \times 10^{13}\,sec^{-1}$ ($\log \varepsilon_1 = 1.73$) and $\nu_2 = 84.5 \times 10^{13}\,sec^{-1}$ ($\log \varepsilon_2 = 1.66$) respectively, where $\nu$ is the frequency and $\varepsilon$ is the molar extinction coefficient.

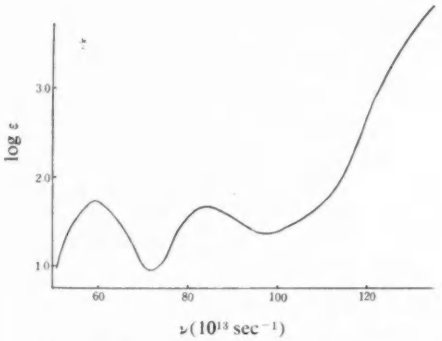



Fig. 2. The absorption spectrum of diaquotetramminecobalt(III) perchlorate.

**Dissociation Pressure of Diaquotetramminecobalt(III) Chloride.**—It was found above that diaquotetramminecobalt(III) chloride decomposed at 70~90°C as follows:

$$[Co(NH_3)_4(OH_2)_2]Cl_3(s) = [Co(NH_3)_4(OH_2)Cl]Cl_2(s) + H_2O(g)$$

The vapor pressure or dissociation pressure of diaquotetramminecobalt(III) chloride was measured at 7~36.5°C with the apparatus already described[8]. The results are listed in Table I.

The logarithm of the dissociation pressure, $p_{mm}$, is plotted against the reciprocal of the absolute temperature in Fig. 3. A straight

Table I. Dissociation pressure of diaquotetramminecobalt(III) chloride

| Temp. °C | $1/T \times 10^3$ | Dissociation pressure $p_{mm}$ | $\log p_{mm}$ |
|---|---|---|---|
| 7 | 3.559 | 4.15 | 0.6181 |
| 19 | 3.425 | 5.40 | 0.7324 |
| 21 | 3.401 | 5.89 | 0.7701 |
| 31 | 3.290 | 6.99 | 0.8445 |
| 36.5 | 3.231 | 7.98 | 0.9020 |

5) M. Mori, M. Shibata, K. Hirota, K. Masuno and Y. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **79**, 1251 (1958).

6) J. V. Quagliano and L. Schubert, *Chem. Revs.*, **50** 201 (1952).

7) M. Mori, R. Tsuchiya and H. Fukuda, This Bulletin, **33**, 1503 (1960).

* By private communication received from R. Tsuchida in Oct., 1959, $\nu_1 = 59.2$ ($\log \varepsilon_1 = 1.72$) and $\nu_2 = 84.6 \sim 84.7$ ($\log \varepsilon_2 = 1.64$).

8) M. Mori and R. Tsuchiya, This Bulletin, **32**, 467 (1959).

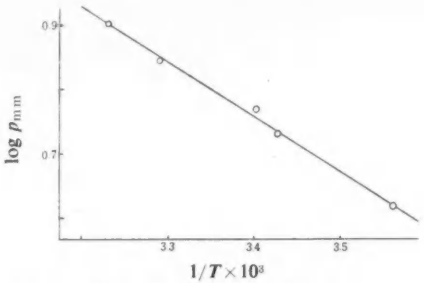



Fig. 3. The relationship between the dissociation pressure of diaquotetramminecobalt(III) chloride and the temperature.

line is obtained. The equation of the straight line is calculated by the method of least squares as,

$$\log p_{mm} = 3.669 - 856.1/T$$

The free energy change for the dissociation is obtained as,

$$\Delta G^\circ = 3916 - 3.604\,T, \quad \Delta G^\circ_{298} = 2842 \text{ cal.} \qquad (1)$$

From the free energy change for the dissociation of hexamminecobalt(III)[8] and aquopentamminecobalt(III) chlorides[9], the free energy change for the reaction in which one gram equivalent of $NH_3$ is replaced by one gram equivalent of $H_2O$ in the coordination sphere is calculated as below:

$$[Co(NH_3)_6]Cl_3(s) + H_2O(g) = [Co(NH_3)_5 \cdot OH_2]Cl_3(s) + NH_3(g)$$
$$\Delta G^\circ = -296 + 8.32\,T \qquad (2)$$

The entropy change is $\Delta S^\circ = -8.32$ e. u. If it is assumed that the entropy change of the reaction,

$$[Co(NH_3)_5OH_2]Cl_3(s) + H_2O(g) = [Co(NH_3)_4(OH_2)_2]Cl_3(s) + NH_3(g) \qquad (3)$$

in which one gram equivalent of $NH_3$ in the reactant is replaced by one gram equivalent of $H_2O$, is equal to the entropy change of the reaction 2, i. e. $-8.32$ e. u., then the free energy change for reaction 3 is obtained by using the value of the above entropy change and the heats of formation of the substances[10,11] concerning the reaction as:

$$\Delta G^\circ = -1140 + 8.32\,T \qquad (4)$$

Since the free energies of formation of aquopentamminecobalt(III) chloride, water vapor and ammonia are known, from these values and Eq. 4 the free energy of formation of diaquotetramminecobalt(III) chloride in the solid state is calculated as,

$$\Delta G^\circ_f = -360600 + 363.2\,T$$
$$\Delta G^\circ_{f298} = -252300 \text{ cal.} \qquad (5)$$

The free energy of formation of aquochlorotetramminecobalt(III) chloride, which is the decomposition product of diaquotetramminecobalt(III) chloride, is obtained from Eqs. 1 and 5 as follows:

$$\Delta G^\circ_f = -298900 + 349.0\,T$$
$$\Delta G^\circ_{f298} = -194900 \text{ cal.}$$

From the above results the free energies of the reaction in which an ammonia molecule is successively replaced by a water molecule in the coordination sphere of hexamminecobalt(III) chloride are calculated and from these relationships it is concluded that the thermodynamic stabilities of these complexes are in the order:

$$[Co(NH_3)_6]Cl_3 > [Co(NH_3)_5OH_2]Cl_3 > [Co(NH_3)_4(OH_2)_2]Cl_3 > [Co(NH_3)_4(OH_2)\cdot Cl]Cl_2 > [Co(NH_3)_5Cl]Cl_2$$

**Infrared Absorption Spectra of Cobalt(III) Aquoammine-complexes.**—The infrared absorption spectra for diaquotetramminecobalt(III) and aquopentamminecobalt(III) perchlorates are listed in Table II together with those for hexamminecobalt(III) perchlorate already reported[12].

From the table it is seen that the wave numbers of the stretching vibration of N–H, $\nu_{N-H}$ for aquo-complexes are lower than those for hexammine-complex, whereas the wave numbers of the degenerate bending vibration, deg. $\delta_{NH_3}$, and the symmetric bending vibration, sym. $\delta_{NH_3}$, of $NH_3$ for the former are higher than those for the latter. The wave numbers of the rocking vibration of $NH_3$, $\rho_{NH_3}$, are remarkably higher for the former. This means that the coordinate bond character of Co—N in the coordination sphere of cobalt(III) ammine-complexes increases when one or two water moleclues coordinate in place of ammonia molecules.

**X-Ray Diffraction Data for Cobalt(III) Aquoammine-complexes.**—Some reports have been published on the X-ray diffraction for

9) M. Mori, R. Tsuchiya and Y. Okano, ibid., 32, 1029 (1959).
10) K. B. Yatsimirskii and L. L. Pankowa, *Zhur. Obshchei Khim.*, 19, 617 (1949); K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 178.
11) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 9.
12) J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, 79, 3295 (1956).

Table II. Wave number of vibration for O-H and N-H bonds in the infrared absorption spectra of hexamminecobalt(III), aquopentamminecobalt(III) and diaquotetramminecobalt(III) perchlorates

| Complex | $\nu_{O-H}$ | $\nu_{N-H}$ | | deg. $\delta_{NH_2}$ | sym. $\delta_{NH_3}$ | $\rho_{NH_3}$ |
|---|---|---|---|---|---|---|
| $[Co(NH_3)_6](ClO_4)_3$ | | 3320 | 3240 | 1630 | 1352 | 803 |
| $[Co(NH_3)_5OH_2](ClO_4)_3$ | 3400 | 3257 | 3205 | 1634 | 1355 | 826 |
| $[Co(NH_3)_4(OH_2)_2](ClO_4)_3$ | 3390 | 3246 | 3195 | 1637 | 1346 | 839 |

Table III. X-Ray diffraction data for aquopentamminecobalt(III) and diaquotetramminecobalt(III) perchlorates

| $[Co(NH_3)_5OH_2](ClO_4)_3$ | | | | $[Co(NH_3)_4(OH_2)_2](ClO_4)_3$ | | | |
|---|---|---|---|---|---|---|---|
| $d$(Å) | $I/I_0$ | $hkl$ | $a$(Å) | $d$(Å) | $I/I_0$ | $hkl$ | $a$(Å) |
| 4.019 | 100 | 220 | 11.37 | 4.001 | 100 | 220 | 11.32 |
| 3.276 | 5 | 222 | 11.35 | | | | |
| 2.842 | 18 | 400 | 11.37 | 2.829 | 20 | 400 | 11.32 |
| 2.319 | 4.3 | 422 | 11.36 | 2.307 | 5.5 | 422 | 11.30 |
| 2.184 | 13 | 333 | 11.35 | 2.174 | 11 | 333 | 11.30 |
| 2.009 | 5 | 440 | 11.36 | 2.000 | 5.5 | 440 | 11.31 |
| 1.796 | 6.5 | 620 | 11.36 | 1.789 | 7 | 620 | 11.31 |
| 1.518 | 6 | 642 | 11.36 | 1.511 | 5.5 | 642 | 11.32 |
| 1.340 | 3 | 822 | 11.37 | | | | |
| | | | $a_{mean}=11.36$ Å | | | | $a_{mean}=11.31$ Å |
| | | | $D=2.087$ | | | | $D=2.119$ |

hexamminecobalt(III) chloride[13] and perchlorate[14], but none for cobalt(III) aquoammine-complexes except $[Co(NH_3)_5(OH_2)]I_3$[15] and $[Co(NH_3)_4(OH_2)_2][TlCl_6]$[16]. The results of the X-ray diffraction measurement for aquopentamminecobalt(III) and diaquotetramminecobalt(III) perchlorates are shown in Table III. In this table $d$ is interplanar spacing, $I/I_0$, relative intensity, and $hkl$, indices of lattice planes.

The crystals of these complexes belong to the cubic system like $(NH_4)_3[FeF_6]$[17] and the number of chemical units in a unit cell is $Z=4$. By comparing the length of the edge of a unit cell, $a$, and the density, $D$, for the above two cobalt(III) aquoammine perchlorates with those for hexamminecobalt(III) perchlorate, $a=11.41$ Å and $D=2.048$[11], as already reported, it is found that the dimension of the unit cell becomes smaller when one gram equivalent of $NH_3$ is replaced by one gram equivalent of $H_2O$ in the coordination sphere of hexamminecobalt-(III) or aquopentamminecobalt(III) perchlorate. Such a tendency can be seen also in the cases of $[Co(NH_3)_6][TlCl_6]$ ($a=11.42$ Å)[18] and $[Co(NH_3)_4(OH_2)_2][TlCl_6]$ ($a=11.30$ Å)[16]. It makes us suppose that the change of the bond distance of Co–N is closely related to the increase of the coordination bond character which can be detected from the infrared absorption spectra.

13) F. M. Jäger, *Z. Kryst.*, **39**, 543 (1904).
14) R. W. G. Wyckoff, S. B. Hendricks and T. P. McCatcheon, *J. Am. Chem. Soc.*, **13**, 389 (1927).
15) G. Natta, *Gazz. chim. ital.*, **58**, 624 (1928).
16) M. Linhard, W. Manthey and K. Plieth, *Z. Elektrochem.*, **57**, 862 (1953).
17) V. Cagliotti and G. Giacomello, *Naturwissenschaften*, **26**, 317 (1938).
18) T. Watanabe, M. Atoji and C. Okazaki, *Acta Cryst.*, **3**, 405 (1950).

**Summary**

The visible and ultraviolet absorption spectra of diaquotetramminecobalt(III) perchlorate were measured and its decomposition process was discussed on the basis of the thermal analytical data.

The decomposition pressure of diaquotetramminecobalt(III) chloride was measured and the free energy of formation of aquochlorotetramminecobalt(III) chloride which was the product of the decomposition was calculated.

The infrared absorption and X-ray diffraction were measured for diaquotetramminecobalt(III) and aquopentamminecobalt(III) perchlorates and the relationships between the dimension of the unit cell and the coordinate bond strength, Co–N, were discussed.

*Department of Chemistry*
*Faculty of Science*
*Kanazawa University*
*Kanazawa*

# *Thermodynamic Studies on Cobalt Complexes. IX. Chemical Equilibrium between Diaquotetramminecobalt(III) Complex and Oxalate Ion**

By Motoshichi MORI, Ryokichi TSUCHIYA and Eisei MATSUDA

(Received December 19, 1961)

The method of Schramm[1] has been well known for a long time as a general method of preparing oxalatotetramminecobalt(III) complexes. It depends on the reaction of oxalic acid upon diaquotetramminecobalt(III), hydroxoaquotetramminecobalt(III), chloroaquotetramminecobalt(III) or carbonatotetramminecobalt(III) complexes. However, the thermodynamic properties of the oxalatotetramminecobalt(III) complex thus formed have never been reported. In order to get information about these properties the chemical equilibrium between diaquotetramminecobalt(III) ion and oxalate ion was studied spectrophotometrically.

## Experimental

Diaquotetramminecobalt(III) complex was prepared as the perchlorate by the reaction of carbonatotetramminecobalt(III) nitrate with perchloric acid. The identity of the sample was confirmed by chemical and thermal analyses, the measurements of the coagulation values and those of absorption spectra[2]. Oxalic acid and potassium and ammonium oxalates were purified by recrystallization.

At first oxalic acid was added to a solution of diaquotetramminecobalt(III) perchlorate as the source of oxalate ion. But the reaction hardly proceeded at all even when the solution was heated. On the other hand, when potassium oxalate was used, the diaquo-complex was decomposed owing to the strong alkalinity of the solution. When ammonium oxalate was used in place of oxalic acid or potassium oxalate, the reaction with diaquotetramminecobalt(III) perchlorate did occur. But, in this case, oxalatotetramminecobalt(III) complex was not produced but cobalt(III) oxalatoammine complex which contained the oxalate ion as an unidentate ligand was obtained. This fact will be described later in detail.

At last, the mixed solution, or the buffer solution, of oxalic acid and potassium oxalate was used. Although the reaction between the buffer solution and diaquotetramminecobalt(III) perchlorate did not proceed at room temperature, it did when heated to 65°C, producing oxalatotetramminecobalt(III) ion.

From the above preliminary experiments the following method of the determination of the chemical equilibrium between the diaquo-complex and oxalate ion was selected. The mixture of 50 ml. of a solution of diaquotetramminecobalt(III) perchlorate and 50 ml. of a buffer solution consisting of oxalic acid and potassium oxalate was kept in the flask at 65°C for ten minutes and then it was immersed in the thermostat at 25°C. When the equilibrium was attained after about six hours, the absorbancy of the solution was measured with a Hitachi EPU-2 type spectrophotometer. The maximum of the first absorption band of diaquotetramminecobalt(III) ion is at $\nu = 59.0 \times 10^{13}\ \mathrm{sec}^{-1}$ ($\log \varepsilon = 1.73$)[2] and that of oxalatotetramminecobalt(III) ion, at $\nu = 58.7 \times 10^{13}\ \mathrm{sec}^{-1}$ ($\log \varepsilon = 1.91$)[3], where $\nu$ is the frequency and $\varepsilon$, the molar extinction coefficient. The measurement of absorbancy of the solution at equilibrium was made at 510 mμ.

Since cobalt(III) oxalato-complexes are readily decomposed by sunlight, a brown flask was employed in order to protect the solution from the photodecomposition. The range of the initial concentration of the diaquotetramminecobalt(III) complex was 1/500~1/800 F and that of the oxalate ion was 1/80~1/5000 F. In order to diminish the ionic strength, the concentration of the diaquo complex must be lowered. But if it is lowered below 1/800 F the error of measurement of the absorbancy will grow larger. Therefore the concentration of the diaquo-complex could not be lowered below 1/800 F. The measurement of pH of the solution was made with a Horiba HRL Model M pH meter.

## Theoretical

The reaction between diaquotetramminecobalt(III) and oxalate ions is expressed by:

$$[Co(NH_3)_4(OH_2)_2]^{3+}(aq.) + C_2O_4^{2-}(aq.) = [Co(NH_3)_4C_2O_4]^{+}(aq.) + 2H_2O(l) \qquad (1)$$

If the initial concentration of the diaquo-complex ion is expressed by $C$, its concentration at equilibrium, by $C_1$ and the concentration of oxalatotetramminecobalt(III) ion at equilibrium, by $C_2$, then

$$C = C_1 + C_2 \qquad (2)$$

If the molar extinction coefficients of the diaquo-complex and oxalate ions at 510 mμ are expressed by $\varepsilon_1$[2] and $\varepsilon_2$[3] respectively, and the value corresponding to the molar extinction coefficient calculated from the absorbancy

* Read at the Symposium on Coordination Compounds of the Chemical Society of Japan, Sendai, September, 1960.

1) W. Schramm, *Z. anorg. u. allgem. Chem.*, **180**, 167, 177 (1929).

2) M. Mori, R. Tsuchiya, S. Takemura and E. Matsuda, This Bulletin, **34**, 1757 (1961).

3) Y. Shimura and R. Tsuchida, ibid., **29**, 312 (1956).

measured at the chemical equilibrium of reaction 1 is expressed by $\varepsilon$, there exists the relationship:

$$C\varepsilon = C_1\varepsilon_1 + C_2\varepsilon_2 \tag{3}$$

From Eqs. 2 and 3, the concentration of each complex ion is obtained by

$$C_1 = C\frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 - \varepsilon_1} \quad \text{and} \quad C_2 = C\frac{\varepsilon - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} \tag{4}$$

In the mixed solution of the diaquo-complex with oxalic acid and potassium oxalate, it is considered that the following three equilibria exist together with the equibrium 1;

$$H_2C_2O_4 \rightleftarrows H^+ + HC_2O_4^- \tag{5}$$

$$HC_2O_4^- \rightleftarrows H^+ + C_2O_4^{2-} \tag{6}$$

$$K_2C_2O_4 \rightleftarrows 2K^+ + C_2O_4^{2-} \tag{7}$$

The first and second dissociation constants of oxalic acid, $K_1$ and $K_2$, are given as follows respectively[4]:

$$K_1 = \frac{C_{H^+} \cdot C_{HC_2O_4^-}}{C_{H_2C_2O_4}} = 5.9\times10^{-2} \quad \text{and}$$

$$K_2 = \frac{C_{H^+} \cdot C_{C_2O_4^{2-}}}{C_{HC_2O_4^-}} = 6.4\times10^{-5}$$

where $C_{H_2C_2O_4}$, $C_{HC_2O_4^-}$, $C_{C_2O_4^{2-}}$ and $C_{H^+}$ are the concentrations of oxalic acid, hydrogenoxalate ion, oxalate ion and hydrogen ion at equilibrium respectively.

The concentrations of the species in the aqueous solution at equilibrium were calculated in the following two cases separately. The first is the case when the concentration of potassium oxalate is relatively small and the oxalate ion in the solution at equilibrium consists of those formed from potassium oxalate by the ionization process 7 and from oxalic acid by process 6. The second is the case when the concentration of potassium oxalate is relatively large and not only the oxalate ion at equilibrium is all formed from potassium oxalate alone but also a part of the hydrogenoxalate ion in process 5 is given by potassium oxalate.

The calculation in the first case is carried out in the following way. The oxalate ion is assumed to consist of those formed by the ionization of potassium oxalate 7 and the second ionization process of oxalic acid 6. So, if the initial concentration of potassium oxalate and the concentration of oxalate ion formed by process 6 are expressed by $C^\circ_{K_2C_2O_4}$ and $C_x$ respectively, the concentration of the oxalate ion at equilibrium is obtained by $C^\circ_{K_2C_2O_4} + C_x - C_2$, since the concentration of the oxalate ion consumed by the reaction with diaquo-complex is $C_2$. When the initial concentration of oxalic acid and the concentration of hydrogenoxalate ion are expressed by $C^\circ_{H_2C_2O_4}$ and $C_y$ respectively, the concentration of the oxalic acid remaining unionized at equilibrium is obtained by $C^\circ_{H_2C_2O_4} - (C_y + C_x)$ and therefore the first and second dissociation constants of oxalic acid are given by the following equations respectively.

$$\left.\begin{aligned} K_1 &= \frac{C_{H^+} \cdot C_y}{C^\circ_{H_2C_2O_4} - (C_y + C_x)} \\ K_2 &= \frac{C_{H^+}(C^\circ_{K_2C_2O_4} + C_x - C_2)}{C_y} \end{aligned}\right\} \tag{8}$$

In these equations, $C^\circ_{H_2C_2O_4}$ and $C^\circ_{K_2C_2O_4}$ are known and $C_2$ is calculated by Eq. 4. The two variables, $C_x$ and $C_y$, can be obtained by solving the above Eq. 8 with respect to $C_x$ and $C_y$ as follows:

$$\left.\begin{aligned} C_x &= \frac{\left(K_1K_2C^\circ_{H_2C_2O_4} + (C_2 - C^\circ_{K_2C_2O_4})\right) \times (C^2_{H^+} + K_1C_{H^+})}{C^2_{H^+} + K_1C_{H^+} + K_1K_2} \\ C_y &= \frac{K_1C_{H^+}(C^\circ_{H_2C_2O_4} + C^\circ_{K_2C_2O_4} - C_2)}{C^2_{H^+} + K_1C_{H^+} + K_1K_2} \end{aligned}\right\} \tag{9}$$

The method of determining $C_{H^+}$ will be described later.

The apparent equilibrium constant, $K_C$, for reaction 1 is given as below,

$$K_C = \frac{C_2 \cdot C^2_{H_2O}}{C_1 \cdot C_{C_2O_4^{2-}}} = \frac{C_2 \cdot C^2_{H_2O}}{C_1(C^\circ_{K_2C_2O_4} + C_x - C_2)} \tag{10}$$

where $C_{H_2O} = 1000/18 = 55.5$. This constant varies with the ionic strength of the solution. The ionic strength must be known to find the thermodynamic equilibrium constant. The concentrations and the ionic strengths of each ion at equilibrium are given as follows:

| | Concentration | Ionic strength |
|---|---|---|
| $[Co(NH_3)_4(OH_2)_2]^{3+}$ | $C_1$ | $(9/2)C_1$ |
| $[Co(NH_3)_4C_2O_4]^+$ | $C_2$ | $(1/2)C_2$ |
| $3ClO_4^-$ | $3(C_1+C_2)$ | $(3/2)(C_1+C_2)$ |
| $H^+$ | $C_{H^+}$ | $(1/2)C_{H^+}$ |
| $K^+$ | $2C^\circ_{K_2C_2O_4}$ | $C^\circ_{K_2C_2O_4}$ |
| $C_2O_4^{2-}$ | $C^\circ_{K_2C_2O_4} + C_x - C_2$ | $2(C^\circ_{K_2C_2O_4} + C_x - C_2)$ |
| $HC_2O_4^-$ | $C_y$ | $(1/2)C_y$ |

The total ionic strength, $\mu$, in the solution is calculated by

$$\mu = 6C_1 + 3C^\circ_{K_2C_2O_4} + 1/2C_{H^+} + 2C_x + 1/2C_y \tag{11}$$

The calculation in the second case is performed in the following manner. In this case the concentration of the oxalate ion ionized by reaction 7 is high enough to combine with

4) R. Gane and Ch. K. Ingold, *J. Chem. Soc.*, **1931**, 2153.

diaquo-complex to form oxalatoammine-complex and to compose a part of hydrogenoxalate ion. When the concentrations of hydrogenoxalate ion produced from potassium oxalate and oxalic acid are expressed by $C_y$ and $C_z$ respectively, the concentrations of hydrogenoxalate ion, unionized oxalic acid and oxalate ion at equilibrium are obtained as $C_y+C_z$, $C^\circ_{H_2C_2O_4}-C_z$ and $C^\circ_{K_2C_2O_4}-C_2-C_y$ respectively and therefore the first and second dissociation constants are given as follows:

$$K_1=\frac{C_{H^+}(C_y+C_z)}{C^\circ_{H_2C_2O_4}-C_z}$$

$$K_2=\frac{C_{H^+}(C^\circ_{K_2C_2O_4}-C_2-C_y)}{C_y+C_z} \qquad (12)$$

The two variables, $C_y$ and $C_z$, can be obtained by solving the above two Eq. 12 as below:

$$C_y=\frac{\left((C^2_{H^+}+K_1C_{H^+})(C^\circ_{K_2C_2O_4}-C_2)\right)-K_1K_2C^\circ_{H_2C_2O_4}}{C^2_{H^+}+K_1C_{H^+}+K_1K_2}$$

$$C_z=\frac{\left(-C^2_{H^+}(C^\circ_{K_2C_2O_4}-C_2)+K_1C_{H^+}\cdot C^\circ_{H_2C_2O_4}+K_1K_2C^\circ_{H_2C_2O_4}\right)}{C^2_{H^+}+K_1C_{H^+}+K_1K_2} \qquad (13)$$

Therefore the concentration of hydrogenoxalate ion at equilibrium, $C_{HC_2O_4^-}$, is given by

$$C_{HC_2O_4^-}=C_y+C_z=\frac{\left(K_1C_{H^+}(C^\circ_{H_2C_2O_4}+C^\circ_{K_2C_2O_4}-C_2)\right)}{C^2_{H^+}+K_1C_{H^+}+K_1K_2} \qquad (14)$$

The apparent equilibrium constant, $K_C$, is given as below:

$$K_C=\frac{C_2\cdot C^2_{H_2O}}{C_1\cdot C_{C_2O_4^{2-}}}=\frac{C_2\cdot C^2_{H_2O}}{C_1(C^\circ_{K_2C_2O_4}-C_2-C_y)} \qquad (15)$$

The total concentrations and the ionic strengths of each ion in this aqueous solution at equilibrium are given as follows:

| | Concentration | Ionic strength |
|---|---|---|
| $[Co(NH_3)_4\cdot(OH_2)_2]^{3+}$ | $C_1$ | $(9/2)C_1$ |
| $[Co(NH_3)_4\cdot C_2O_4]^+$ | $C_2$ | $(1/2)C_2$ |
| $3ClO_4^-$ | $3(C_1+C_2)$ | $(3/2)(C_1+C_2)$ |
| $H^+$ | $C_{H^+}$ | $(1/2)C_{H^+}$ |
| $K^+$ | $2C^\circ_{K_2C_2O_4}$ | $C^\circ_{K_2C_2O_4}$ |
| $C_2O_4^{2-}$ | $C^\circ_{K_2C_2O_4}-C_2-C_y$ | $2(C^\circ_{K_2C_2O_4}-C_2-C_y)$ |
| $HC_2O_4^-$ | $C_y+C_z$ | $(1/2)(C_y+C_z)$ |

The total ionic strength, $\mu$, in the solution is calculated by

$$\mu=6C_1+3C^\circ_{K_2C_2O_4}+1/2\,C_{H^+}-2C_y+1/2(C_y+C_z) \qquad (16)$$

## Results and Discussion

At first by measuring the absorbancy of the solution at equilibrium, the concentrations of diaquoammine complex and oxalatoammine-complex, $C_1$ and $C_2$, were calculated by Eq. 4. By using these values, the initial concentrations of oxalic acid and potassium oxalate, $C^\circ_{H_2C_2O_4}$ and $C^\circ_{K_2C_2O_4}$, the values of the first and second dissociation constants of oxalic acid, $K_1$ and $K_2$, and, by using the activity of hydrogen ion, $a_{H^+}$, in place of the concentration, $C_{H^+}$, the approximate concentrations of oxalic acid and hydrogenoxalate ion, $C_x$ or $C_y$, were estimated by Eq. 9 or 13. The approximate ionic strengths of the solution at equilibrium were also calculated by Eq. 11 or 16.

In order to know the true concentrations of oxalate and hydrogenoxalate ions, the above calculation must be carried out by using the concentration of hydrogen ion. In spite of it the value obtained by pH measurement is not the concentration of hydrogen ion but the activity. Therefore by finding the activity coefficient of hydrogen ion in each solution having the above approximate ionic strengths from Kielland's table[5], the concentration of hydrogen ion was obtained and the concentrations of oxalate ion and hydrogenoxalate ion and the ionic strengths were again calculated by Eqs. 9 and 11 or 13, 14 and 16 respectively.

Then the apparent equilibrium constant, $K_C$, was calculated by Eq. 10 or 15. These values calculated are all summarized in Table I.

The logarithm of the apparent equilibrium constant, $K_C$, is plotted against the square root of the ionic strength, $\mu$, in Fig. 1. If it is assumed that this plotting gives a quadratic curve, the equation of the curve is calculated by the method of least squares as,

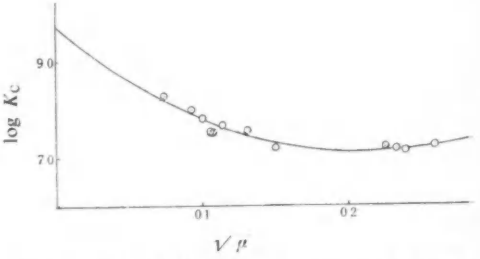



Fig. 1. The relationship between the apparent equilibrium constant of the reaction, $[Co(NH_3)_4(OH_2)_2]^{3+}+C_2O_4^{2-}=[Co(NH_3)_4C_2O_4]^+ +2H_2O$, and the ionic strength in the solution.

5) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

Table I. Equilibrium of $[Co(NH_3)_4(OH_2)_2]^{3+}+C_2O_4^{2-}=[Co(NH_3)_4C_2O_4]^{+}+2H_2O$, at 25°C
Measurement of extinction coefficient was made at $\lambda=510$ mμ.

| Initial concn. of $[Co(NH_3)_4(OH_2)_2](ClO_4)_3$ $C\times10^3$ F | Initial concn. of $H_2C_2O_4$ $C_{H_2C_2O_4}\times10^3$ F | Initial concn. of $K_2C_2O_4$ $C_{K_2C_2O_4}\times10$ F | $\varepsilon$ | $C_1\times10^3$ | $C_2\times10^3$ |
|---|---|---|---|---|---|
| 1.250 | 1.250 | 1.250 | 76.3 | 0.225 | 1.025 |
| 1.250 | 0.500 | 0.500 | 67.0 | 0.648 | 0.603 |
| 2.00 | 2.00 | 2.00 | 75.9 | 0.393 | 1.607 |
| 1.250 | 2.50 | 2.50 | 78.8 | 0.112 | 1.138 |
| 2.00 | 1.00 | 1.00 | 68.2 | 0.946 | 1.114 |
| 2.00 | 0.667 | 0.667 | 63.7 | 1.275 | 0.725 |
| 2.00 | 0.500 | 0.500 | 62.0 | 1.395 | 0.605 |
| 2.00 | 3.125 | 3.125 | 71.5 | 0.550 | 1.450 |
| 2.00 | 6.250 | 6.250 | 75.5 | 0.422 | 1.578 |
| 2.00 | 12.50 | 12.50 | 72.0 | 0.675 | 1.325 |
| 10.00 | 10.00 | 10.00 | 70.0 | 3.17 | 6.83 |
| 10.00 | 10.00 | 10.00 | 68.0 | 3.74 | 6.26 |
| 2.00 | 25.00 | 25.00 | 75.0 | 0.354 | 1.646 |
| 10.00 | 20.00 | 20.00 | 73.9 | 2.08 | 7.92 |

| pH | $C_{H^+}\times10^3$ | $C_{C_2O_4^{2-}}\times10^4$ | $K_C\times10^{-7}$ | log $K_C$ | $\mu$ | $\sqrt{\mu}$ |
|---|---|---|---|---|---|---|
| 3.00 | 1.076 | 0.814 | 17.24 | 8.237 | 0.005352 | 0.0732 |
| 3.42 | 0.412 | 0.511 | 5.608 | 7.748 | 0.006065 | 0.0779 |
| 3.00 | 1.089 | 0.131 | 9.614 | 7.983 | 0.008379 | 0.0915 |
| 2.91 | 1.33 | 0.174 | 17.99 | 8.255 | 0.008602 | 0.0928 |
| 3.12 | 0 829 | 0.627 | 5.785 | 7.762 | 0.009850 | 0.0993 |
| 3.24 | 0.629 | 0.557 | 3.144 | 7.497 | 0.01047 | 0.1023 |
| 3.36 | 0.478 | 0.463 | 2.885 | 7.460 | 0.01059 | 0.1029 |
| 2.80 | 1.75 | 1.642 | 4.945 | 7.694 | 0.01278 | 0.1131 |
| 2.70 | 2.23 | 2.95 | 3.904 | 7.592 | 0.01665 | 0.1290 |
| 2.65 | 2.62 | 5.45 | 1.109 | 7.045 | 0.02162 | 0.1470 |
| 2.67 | 2.50 | 3.20 | 2.074 | 7.317 | 0.05073 | 0.225 |
| 2.67 | 2.50 | 3.30 | 1.562 | 7.194 | 0.05330 | 0.231 |
| 2.63 | 2.74 | 10.55 | 1.357 | 7.133 | 0.05650 | 0.238 |
| 2.60 | 2.97 | 6.50 | 1.804 | 7.256 | 0.06606 | 0.257 |

$$\log K_C=65.24\,\mu-25.98\sqrt{\mu}+9.687$$

The value of log $K_C$ at $\sqrt{\mu}=0$ is obtained by the extrapolation of this curve as,

$$\log K=9.7$$

This is the thermodynamic equilibrium constant of the reaction between diaquotetramminecobalt(III) and oxalate ions. The free energy change of the reaction is obtained as,

$$\Delta G^\circ_{298}=-13.2\text{ kcal.} \qquad (17)$$

Since the free energies of formation of diaquotetramminecobalt(III) ion, oxalate ion and water in unit activity are known as −152.8 kcal.[6], −161.8 kcal.[7] and −56.69 kcal.[8] respectively, the free energy of formation of oxalatotetramminecobalt(III) ion in unit activity is calculated as

$$\Delta G^\circ_{f\,298}=-213.9\text{ kcal.}$$

The heat of reaction between diaquotetramminecobalt(III) and oxalate ions is calculated as,

$$\Delta H=6.8\text{ kcal.} \qquad (18)$$

by using the heats of reaction of each compound concerned, i. e., −235.7 kcal.[9] for diaquotetramminecobalt(III) ion, −197.0 kcal.[7] for oxalate ion, −68.32 kcal.[8] for water and −289.3 kcal. for oxalatotetramminecobalt(III) ion. The last value is estimated from $\Delta H=-146.0$ kcal.[10] for hexamminecobalt(III) ion

6) A. B. Lamb and A. T. Larson, ibid., 42, 2038 (1920).
7) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 120.
8) F. D. Rossini et al., l. c., p. 9.
9) K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 178.
10) K. B. Yatsimirskii, l. c., p. 161.

and $\Delta H = -575.8$ kcal.[11] for trisoxalatocobaltate(III) ion. By using 17 and 18 the entropy change for the reaction between diaquotetrammine cobalt(III) and oxalate ions is obtained as

$$\Delta S = 67.1 \text{ e. u.}$$

This large value suggests the great stability of oxalatotetramminecobalt(III) ion due to the chelate formation by oxalate ion.

The absorbancy of the solution produced by the reaction of diaquotetramminecobalt(III) perchlorate with ammonium oxalate was measured, and the spectra of the solution are shown in Fig. 2. The absorption spectra of oxalatopentamminecobalt(III) ion and oxalatotetramminecobalt(III) ion are also shown in the same figure. It is found that the absorption spectra of the compound produced at room temperatures by the reaction of the diaquo-complex with ammonium oxalate resembles that of oxalatopentamminecobalt(III) ion, whereas, when the reaction is promoted upon heating to 60°C, a shoulder of the absorption curve appears in the range of wavelengths corresponding to the second absorption band of oxalatotetramminecobalt(III) ion. It is presumed that a part of oxalate ion coordinated as a unidentate ligand at room temperatures undergoes transition to a bidentate ligand.

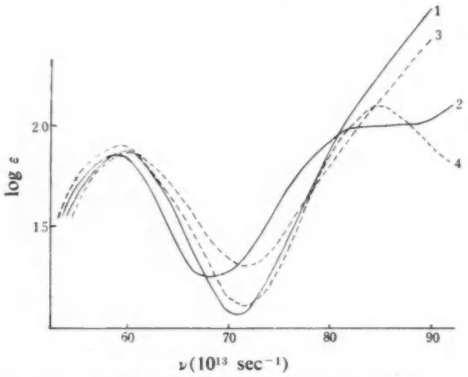



Fig. 2. The absorption spectra of the solution containing diaquotetramminecobalt(III) perchlorate and ammonium oxalate.
1. The solution at room temperature.
2. The solution after being heated at 60°C.
3. Oxalatopentamminecobalt(III) perchlorate.
4. Oxalatotetramminecobalt(III) perchlorate.

11) K. B. Yatsimirskii and L. L. Pankowa, *Zhur. Obshchei Khim.*, **19**, 623 (1949); K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 180; *Chem. Abstr.*, **43**, 7805 *d* (1949).


## Summary

The equilibrium of the reaction, $[Co(NH_3)_4(OH_2)_2]^{3+} + C_2O_4^{2-} = [Co(NH_3)_4C_2O_4]^{+} + 2H_2O$ (1), was measured spectrophotometrically and the free energy of formation of oxalatotetramminecobalt(III) ion was calculated. The large increase of the entropy for the above reaction was interpreted by the chelate effect of oxalate ion.

When the mixture of oxalic acid and potassium oxalate reacts with diaquotetramminecobalt(III) complex, oxalate ion is coordinated as a bidentate ligand, whereas it is coordinated as an unidentate ligand when ammonium oxalate reacts with the same diaquo-complex.


*Department of Chemistry*
*Faculty of Science*
*Kanazawa University*
*Kanazawa*

# *Chemical Studies on Radioactive Indicators. XXIV. Separation of Rhenium from Technetium by the Distillation Method*

By Mutsuo KOYAMA

(Received December 22, 1960)

It has been considered that technetium has much resemblance in chemical properties to rhenium and the latter element has often been used as a carrier in the analysis of the former. An appropriate method is needed for the separation and the determination of technetium which is supposed to be present in natural ores or meteorites and also for the preparation of carrier-free rhenium or technetium produced by the bombardment of nuclear particles. Although several methods for separation, i. e., precipitation method[1], ion exchange method[2] and paper chromatography[3] have been proposed, it can not be said that any one of them is satisfactory in the analysis of the samples containing technetium and rhenium over a wide range of quantity.

The distillation of rhenium as $Re_2O_7$[4,5] has been a powerful method in the isolation from various elements other than technetium but the attempt to separate rhenium from technetium has not appeared yet.

In the previous paper[6], the author pointed out that the distillation of technetium from sulfuric acid is promoted by the addition of an oxidizing agent, such as nitric acid or potassium bichromate, and delayed by the addition of a reducing agent, such as hydroxylamine.

The resistance for the distillation of technetium in the presence of a reducing agent would be due to the formation of a lower oxidation state than +7. A similar experiment was performed on rhenium and it was found that reducing agent showed no effect on the distillation.

In this experiment, several kinds of gas were passed through the distilling flask as carrier and it was found that steam was the most effective on the separation of rhenium from technetium. The experiments were carried out with the solutions of carrier-free $^{95m}Tc$, $^{97m}Tc$, $^{183}Re$ and $^{184}Re$ in the presence or the absence of rhenium carrier.

The results were quite satisfactory as shown in Tables I and II.

## Experimental

**Reagents and Apparatus.**—*Isotopes.*—$^{95m}Tc$(60d) and $^{97m}Tc$(90d) were isolated as pertechnetate, from the proton-bombarded molybdenum target[6]. $^{183}Re$(71d) and $^{184}Re$(50d) were isolated as perrhenate from the proton-bombarded tungsten target[7].

*Stable Rhenium.*—Metallic powder of rhenium was obtained from Yokozawa Chemicals Co. and was converted to perrhenate by fusing it with sodium hydroxide and sodium peroxide in a nickel crucible.

*Distilling Apparatus.*—A pyrex glass distilling apparatus shown in Fig. 1 was prepared. Junctions were connected without grease.

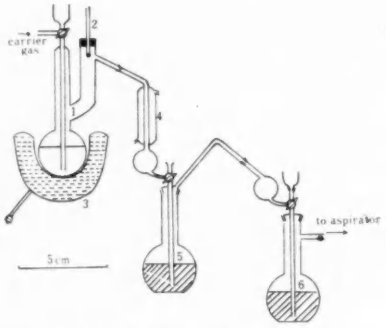



Fig. 1. Distilling apparatus.
1. Distilling flask 2. Thermometer
3. Mantle heater 4. Cooler
5. Receiver-1 (10 ml. of water)
6. Receiver-2 (20 ml of 4 N NaOH)

*Counters.*—A single channel $\gamma$-ray spectrometer (crystal: NaI(Tl), 1×1 inch) made by Kobe Kogyo Co., Ltd. and a G. M. counter (Tube: G. M. 132A, mica window 1.95 mg./cm$^2$) made by Metro Denki Co., Ltd. were used.

**Procedure.**—Six milliliters of the sample solution was taken in the distilling flask and heated with a mantle heater whose temperature was controlled with a transformer.

Carrier gas was conducted at the rate of 60

1) C. Perrier and E. Segrè, *J. Chem. Phys.*, **5**, 712 (1937).
2) E. Jacobi, *Helv. Chim. Acta*, **61**, 2118 (1948).
3) M. Lederer, *Anal. Chim. Acta*, **12**, 146 (1955).
4) W. Geilmann and E. Weibke, *Z. anorg. u. allgem. Chem.*, **199**, 120 (1931).
5) W. Geilmann and H. Bode, *Z. anal. Chem.*, **130**, 323 (1950).
6) M. Ishibashi, T. Fujinaga and M. Koyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1260 (1960).
7) M. Ishibashi, T. Fujinaga and M. Koyama, ibid., **82**, 185 (1961).

bubbles per minute. Receivers were cooled with ice water, whenever necessary. Any adhering activity inside the cooler was washed out into the receiver with a small amount of water before the measurements of the activities of the distillate. All the solutions were brought to a known volume in a volumetric flask and an aliquot was taken in a 5 ml. glass counting dish and was mounted for the $\gamma$-ray measurement.

## Results and Discussion

**Effect of the Concentration of Sulfuric Acid.** —Carrier-free rhenium was used in the experiments for testing the effect of the concentration of sulfuric acid on the distillation of rhenium. Rhenium was not distilled out from the pure water solution. On heating the sulfuric acid solution, the temperature remained at about 98~100°C during the distillation of water. After the water was distilled over, the temperature decreased once and again rose gradually to about 250°C, while sulfuric acid began to be distilled. The distilling temperature (250°C) was changeable depending on the heating and bubbling conditions.

In Fig. 2, the amounts of distilled rhenium are plotted against the amounts of distilled sulfuric acid. When 60% of the total amount of sulfuric acid was distilled, nearly 100% of rhenium was distilled out, irrespective of the initial concentration of sulfuric acid. The rate of distillation of rhenium was the greatest with 6 N sulfuric acid and the smallest with 30 N sulfuric acid. However, no quantitative distillation could be expected by the use of dilute sulfuric acid, because the volume of distilling solution became too small to dissolve the residual materials in the course of distillation.

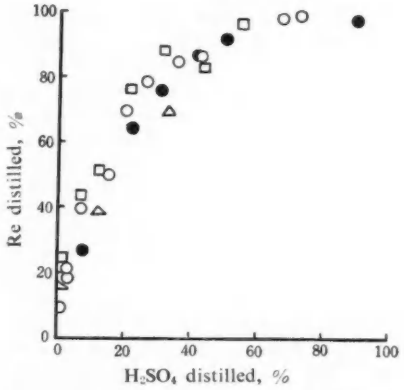



Fig. 2. Relationship between amount of Re distilled and that of $H_2SO_4$.
△ 6 N $H_2SO_4$ ○ 18 N $H_2SO_4$
□ 24 N $H_2SO_4$ ● 30 N $H_2SO_4$

Therefore, 18 N sulfuric acid was used in the following experiments.

**Effects of Reducing Agent and Carrier Gas on the Distillation of Rhenium and Technetium.** —In order to examine the effects of the atmosphere in the distilling flask on the distillation rate of rhenium and technetium, three kinds of gas, i.e., air, hydrogen and carbon dioxide, were bubbled respectively through the flask during the distillation.

Stannous chloride and hydroxylamine were used as the reducing agent, but the former

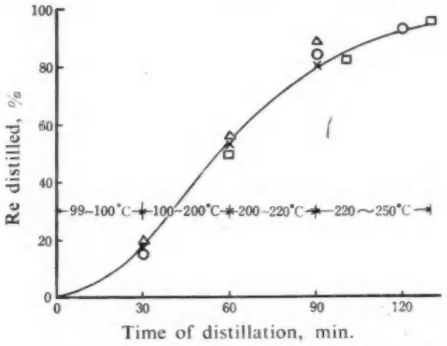



Fig. 3. Distillation rate of Re from 18 N $H_2SO_4$ in the presence or the absence of reducing agents.

| | Reducing agent | Carrier gas |
|---|---|---|
| ○ | None | Air |
| □ | 〃 | $CO_2$ |
| × | 10% $SnCl_2$ 1 ml. | 〃 |
| △ | 10% $NH_2OH \cdot HCl$ 1 ml. | 〃 |

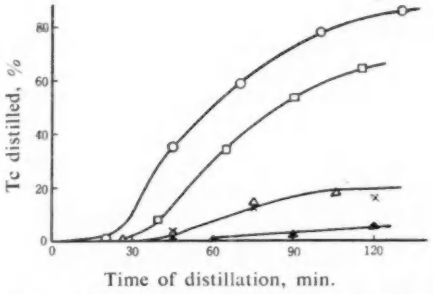



Fig. 4. Distillation rates of Tc from 18 N $H_2SO_4$ in the presence or the absence of reducing agents.

| | Reducing agent | Carrier gas |
|---|---|---|
| ○ | None | Air |
| □ | 10% $NH_2OH \cdot HCl$ 0.5 ml. | 〃 |
| △ | 〃 | $CO_2$ |
| × | 〃 | $H_2$ |
| ▲ | 10% $NH_2OH \cdot HCl$ 2 ml. | $CO_2$ |

TABLE I. DISTILLATION RATES OF RHENIUM

| Solution | Redistilled (%) at various times | | | | | | |
|---|---|---|---|---|---|---|---|
| | 20 min. | | 40 min. | | 60 min. | | Spot tests of residual solution |
| | c.p.m. | % | c.p.m. | % | c.p.m. | % | |
| Carrier-free Re alone | 3570<br>3790 | 61.6<br>65.4 | 5540<br>5250 | 95.6<br>90.5 | 5780<br>5740 | 99.8<br>98.9 | — |
| Carrier-free Re + 10% $NH_2OH$·HCl 2 ml. | 3210 | 55.4 | 5170 | 89.2 | 5790 | 99.9 | — |
| Re 1 mg. + 10% $NH_2OH$·HCl 2 ml. | 2450<br>3090 | 42.2<br>53.2 | 5200<br>5480 | 89.6<br>94.5 | 5780<br>5790 | 99.7<br>99.8 | None<br>None |
| Re 10 mg. + 10% $NH_2OH$·HCl 2 ml. | 890<br>2200 | 15.4<br>38.2 | 5450<br>5220 | 94.5<br>90.7 | 5740<br>5790 | 99.0<br>99.9 | 1γ>Re<br>1γ>Re |

* Carrier gas: steam, Total volume of solution to be distilled: 6 ml. of 18 N $H_2SO_4$, Radioactive Re added: 5800 c.p.m.

TABLE II. DISTILLATION RATES OF TECHNETIUM

| Solution | Tc distilled (%) at various times | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 20 min. | | 40 min. | | 60 min. | | 80 min. | | 100 min. | |
| | c.p.m. | % | c.p.m. | % | c.p.m. | % | c.p.m. | % | c.p.m. | % |
| Tc alone | 4470<br>628 | 12.4<br>16.6 | 704<br>784 | 18.6<br>20.7 | 765<br>832 | 20.2<br>22.0 | 795<br>835 | 21.0<br>22.0 | — | — |
| Tc + 10% $NH_2OH$·HCl 2 ml. | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 20<br>10 | 0.5<br>0.3 | — | — |
| Tc + Re 10mg + 10% $NH_2OH$·HCl 2 ml. | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | — | — |
| Tc + $HNO_3$ 1 ml. | 1470<br>1360 | 38.8<br>35.0 | 2000<br>2360 | 52.8<br>62.3 | 2020<br>2380 | 53.0<br>63.0 | 3090<br>3190 | 81.7<br>84.5 | 3500<br>3350 | 92.4<br>88.6 |

* At the same condition as in the case of rhenium.
Tc added: 3800 c.p.m.

was partially distilled out. In Fig. 3, it can be seen that the distillation rate of rhenium from sulfuric acid is independent of the presence of hydroxylamine and bubbling gas. The fact that the addition of hydroxylamine had no effect on the distillation rate of rhenium shows that hydroxylamine can not reduce perrhenate[8].

In the case of technetium, the decrease in the distillation rate was distinctly observed by the addition of hydroxylamine, even when air was used as carrier gas.

In the same experiment, the bubbling of hydrogen or carbon dioxide caused a marked decrease in the distillation rate, especially in the period of the distillation of water, little technetium being found in the receiver.

The difference of the distillation rates between the use of air and that of carbon dioxide or hydrogen seems to be due to the difference of oxidizing ability against hydroxylamine. After the water was consumed in the flask, technetium gradually came to appear in the distillate. The increase in the amounts of hydroxylamine caused the decrease of the distillation rate of technetium.

**Separation of Rhenium from Technetium.**— In the foregoing method, as an appreciable amount of hydroxylamine is decomposed by heating with sulfuric acid solution, much hydroxylamine has to be added for the quantitative separation of rhenium from technetium.

To achieve smooth distillation, it is desirable to keep the amount of hydroxylamine as small as possible. Utilizing the fact that much rhenium but no technetium could be found in the distillate, the steam distillation method in the presence of hydroxylamine was examined.

Table I shows the distillation rates of rhenium obtained by steam distillation in the presence or the absence of hydroxylamine. It was found that by passing steam only at 100°C, little rhenium was distilled out, however, with gentle heating of the flask above 105°C, rhenium came to be distilled out with the steam.

8) S. Tribalat, *Ann. chim.*, **4**, 289 (1949).

After distillation for 60 min., more than 99% of the rhenium was recovered. In the case when the distillation was carried out with stable rhenium, a spot test for the rhenium[9] remaining in the flask proved to be less than 1$\gamma$ of rhenium as shown in Table I.

The presence of hydroxylamine also had no effect on the distillation rate of rhenium in this method. In Table II, the distillation rates of technetium in the same condition as in the case of rhenium are shown. Distillation rates of technetium from 18 N sulfuric acid were smaller than that of rhenium even in the absence of hydroxylamine. In the presence of hydroxylamine no technetium appeared in the receivers, while most of the rhenium had been distilled off.

On the other hand, it was also observed that the presence of nitric acid promoted the distillation of technetium in the steam distillation. Therefore the separation of rhenium from technetium followed by the separation of technetium from other non-volatile materials by the distillation method could be attained by the proper use of hydroxylamine and nitric acid.

9) E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York (1959), p.754.

**Summary**

The separation of rhenium from technetium was investigated. Pertechnetate is reduced to non-volatile species by the use of hydroxylamine, but perrhenate is not reduced by such an agent. Rhenium is distilled out with steam from sulfuric acid medium and technetium remains in the solution containing hydroxylamine. Rhenium from carrier-free amounts up to 10 mg. can be separated quantitatively from technetium by this method.

The author desires to express his hearty thanks to Professor Masayoshi Ishibashi and Professor Taitiro Fujinaga for their helpful advice and encouragement throughout this work. The author is also grateful to Dr. Kazuo Saito of the Institute for Nuclear Study, the University of Tokyo, for making preparation of radio-isotopes convenient.

*Chemistry Institute*
*Faculty of Science*
*Kyoto University*
*Sakyo-ku, Kyoto*

# *Chemical Use of the Absorption of Soft $\gamma$-Rays, $\beta$-Ray-excited X-Rays and K-Capture X-Rays*. I. Improvement in Fundamental Technique and Introduction of a Differential Absorption Method*

By Tadashi NOZAKI

(Received December 20, 1960)

Soft $\gamma$-rays, $\beta$-ray-excited X-rays and K-capture X-rays are absorbed mainly by the photoelectric effect in most cases, the absorption coefficient depending much on the atomic number of the absorber material. The mass absorption coefficient ($\sigma$) for the photoelectric absorption of a photon whose energy is over the absorption edge of the absorber material is expressed by[1]

$$\sigma = C(Z^5/A)E^{-\lambda} \qquad (8/3 < \lambda < 7/2) \quad (1)$$

where $Z$ and $A$ are respectively the atomic number and the atomic weight of the absorber material and $C$ is a constant.

This phenomenon is to be applied to a vast field of chemistry as well as radiography. Recently, several kinds of works by the use of the absorption of such photons have been published[2-4], including the determination of sulfur in petroleum, of chlorine and bromine in solid organic substances, and of uranium and heavy metal salts. The thickness and density of several kinds of material were also measured by similar techniques. The fundamental technique which has been adopted in these works, however, is useful only for either of the following two cases; (1) when a monoenergetic photon-beam source of a suitable

* A part of this paper was reported at the 2nd Isotope Conference of Japan, February, 1958.

1) e. g., E. Segrè, "Experimental Nuclear Physics", Vol. I, John Wiley & Sons, Inc., New York (1953), p. 310.

2) W. W. Meinke, *Anal. Chem.*, **28**, 737 (1956).
3) W. W. Meinke, ibid., **30**, 688 (1958).
4) W. W. Meinke, ibid., **32**, No. 5-106R (1960).

energy is used (i.e. when the exponential absorption law holds), and (2) when a relationship between the absorbance and the quantity (or concentration) of the element (or substance) to be determined can easily be obtained empirically under a given condition.

To extend the applicability of the absorption phenomenon, according to the present author's opinion, it is essential to improve the fundamental technique so that an exponential absorption curve and an accurate absorption coefficient could be obtained for a photon-beam even when it is not exactly mono-energetic.

Thus, the following studies have been undertaken: (1) examination of a source giving photons of required energy, (2) examination of a detector which enables an efficient measurement of the radiation and gives an absorption curve as near as possible to the exponential with a given absorber, (3) introduction of the differential absorption method which is useful for obtaining a better absorption curve and a more accurate absorption coefficient in the presence of photons of different energies, (4) examination of apparent change in the absorption coefficient with geometrical arrangement, and (5) establishment of an empirical relationship between the absorption coefficient and the photon energy.

**Photon-beam Source.** — Absorptiometry in quantitative analysis is usually based on Lambert-Beer's law, regardless of the photon-beam energy (wavelength). For a mono-energetic photon-beam an exponential absorption curve can be obtained easily. Radio-isotopes emitting such photons are desirable as the source, and have been used in several works[2-4]. Various nuclides including the following are useful for this purpose: $^{51}$Cr, $^{133}$Ba, $^{203}$Hg, $^{139}$Ce, $^{141}$Ce, $^{185}$W, $^{153}$Gd, $^{97m}$Tc, $^{170}$Tm, $^{109}$Cd, $^{204}$Tl, $^{241}$Am, $^{145}$Sm, $^{73}$As, $^{210}$Pb (RaD), $^{125}$I, $^{93}$Mo, $^{68}$Ge, $^{59}$Ni, $^{55}$Fe and $^{49}$V. (The photon energy decreases in the order given.) In using a radio-isotope emitting also $\beta$-rays for the source, the Bremsstrahlung should be made as weak as possible with a suitable enveloping substance (e.g. polystyrene).

Since a relatively small number of nuclides among those written above are usually accessible, another kind of source, generating $\beta$-ray-excited X-rays, is required for increasing the energy variety. With $\beta$-ray-excited X-rays as the source, such improvements in the fundamental technique as shown later are necessary, as they are not exactly mono-energetic. The yield and the purity (absence of photons of unsuitable energies) depend on the target (converter) and the arrangement of the generator. For the present purpose the purity of the X-rays and the ease in the change of the target material are more important than the yield. A reflection-type generator with a $K_\beta$-filter holder, (Fig. 1) serves conveniently.

Figure 2 shows the spectra observed by a scintillation counter (sodium iodide $1'' \times 1''$ crystal with aluminum cover), and Fig. 3 those by the scintillation and a proportional counter.

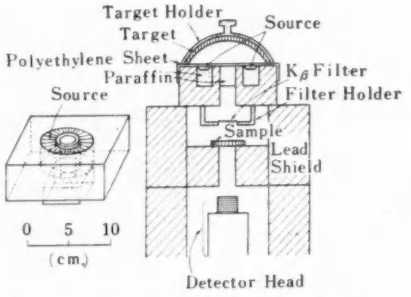



Fig. 1. Generator of $\beta$-ray-excited X-rays.

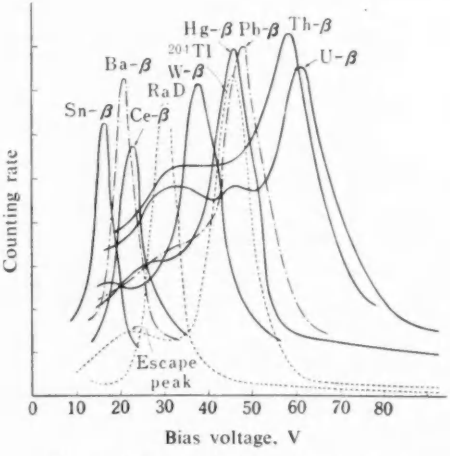



Fig. 2. Spectra of photon-beam sources.

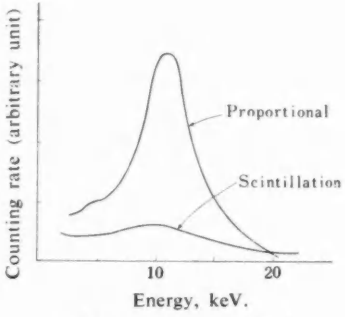



Fig. 3. Spectra of Br-$\beta$.

(For convenience, β-ray-excited X-ray of element M is written as M-β in this paper.)

**Detector.** — The counting efficiency and the shape of the absorption curve depend much on the detection method. When $^{55}$Fe is used as a source, a simple G-M counter works satisfactorily. But this counter is a poor detector for a photon-beam having a higher energy than 10 keV. and the pulse height cannot be discriminated. Thus, an ordinary G-M counter can be used only for a few sources: e. g. $^{55}$Fe, $^{59}$Ni.

Measurement of photon-beams by counting only a narrow region of photo-peak (photo-peak counting) by a low-noise scintillation counter with a single channel analyzer offers a better result in general; the efficiency is high for photons of 20 to 300 keV. and the absorption curve is more similar to a typical exponential curve. For a photon having an energy under 20 keV., however, the following three problems are encountered: (1) the absorption by the cover of the scintillator, (2) the multiplier noise, and (3) the broadening of photo-peak (e. g. those in Fig. 2). The first can be made small by the use of a beryllium-covered crystal, which, however, is not always readily available. On the other hand, a proportional counter tube filled with xenon, krypton or a mixture of these serves, as a still better detector for such a measurement. Fig. 3 shows the spectra of Br-β measured by a xenon-filled proportional counter and by the scintillation counter. No marked photo-peak is observed by the latter. Though the photo-peak obtained by the proportional counter is not so sharp as inferred from literature[5], probably owing to the end effect, the counter is proved to be a very useful detector for such a photon-beam. A krypton-filled tube works as either a proportional or a G-M counter according to the applied voltage, though the dead time of the G-M tube is as long as 1 millisecond. By the use of an external quenching circuit, however, such a tube could be used also as a G-M tube and provides a cheaper technique for measuring photons below 50 keV.

In Fig. 4 the absorption curves of photon-beam from $^{201}$Tl and of Hg-β are shown. Both emit the characteristic X-rays of mercury. The curve measured by a usual G-M counter is far from the exponential curve; the absorption coefficients are much larger at the initial stage, and an absorption tail is observed. The former phenomenon can be attributed to the L-series X-rays which are more sensitive to counter than the *K* X-rays. The same is seen

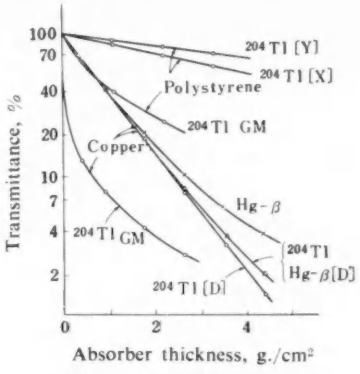



Fig. 4. Absorption curves.

GM; Measured by a G-M counter
[D]; The differential absorption curve
[X]; Absorber at the position in Fig. 1
[Y]; Absorber on the scintillator

with $^{203}$Hg, which emits a γ-ray and characteristic X-rays of thallium owing to internal conversion. The tailing should be due to the Bremsstrahlung. The curves obtained by the photo-peak counting with a scintillation counter are greatly superior. For $^{203}$Hg, the curve maintains the exponential form even when the counting rate decreases to 1/1000 of the initial. For other sources, especially for β-ray-excited X-rays, however, the absorption tailing exists to a considerable degree.

The energy resolution of the counter should be taken into account, since $K_\alpha$ X-rays of the β-ray-excited X-ray are always accompanied with $K_\beta$ rays and Bremsstrahlung of similar energies. On measuring a mono-energetic photon-beam by a scintillation or a proportional counter, the photo-peak is expressed by the Gaussian distribution curve,

$$R = k \exp[-h^2(E_m - E)^2] \qquad (2)$$

where $R$ is the counting rate, $E$ is the energy, $E_m$ is the observed energy giving maximum $R$ on the spectrum, and $k$ and $h$ are constants. And,

$$(\Delta E)_{1/2} = C\sqrt{E_m} \qquad (3)$$

where $(\Delta E)_{1/2}$ is the full width of photo-peak at 1/2 counting rate and $C$ is a constant. By the use of a good source, i. e. RaD, the value $C$ in Eq. 3 can be determined, and from this value and Eq. 2 the fraction of $K_\beta$ involved in the measurement range is calculated under a given experimental condition. For a common experimental condition described in the experimental part, the effect of $K_\beta$ is usually of less significance in case of a source giving a higher

5) W. Parrish et al., *Rev. Sci. Instr.*, **27**, 795 (1956).

energy than Hg-$\beta$, but must be considered for a source giving a lower energy than Ce-$\beta$. In the latter case a $K_\beta$ filter is useful to some extent; the shape in a higher energy region than the top of the photo-peak is improved and the photo-peak itself becomes sharper.

**Differential Absorption Method.** — As mentioned above, the absorption curve obtained by the above technique is in general not entirely satisfying for an accurate work. Inevitably there is absorption tailing to a certain degree, which is a nuisance when trying to obtain an accurate absorption coefficient, especially when the absorbance is large.

Two useful methods for the removal of the effect of absorption tailing (differential method and auxiliary absorption method) are presented, which have been devised anew in consideration of the causes of the tailing.

There must be three causes:

(1) Photons of a higher energy suffer the Compton scattering in the detector and escape with an energy loss in the vicinity of the measurement range.

(2) The same scattering also occurs in the absorber and surrounding materials, and a part of the scattered photons can have a similar energy as that of the main photo-peak and enter the detector.

(3) The escape-peak of a photon whose energy is higher by the energy of the $K_\alpha$ of the detector material appears in the measurement range.

For effects 1 and 2, the following relationship is known[6].

$$E_e = h\nu_0 \frac{2h\nu_0/mc^2}{1+2h\nu_0/mc^2} \tag{4}$$

where $E_e$ is the maximum energy that an electron can obtain after a collision. When $E_e$ is smaller than $mc^2/5$, $h\nu_0/E_e$ is greater than 7/2. This relathionship shows that photons giving the effect 1 must have had much higher energies than the observed range, when the photons were subjected to only one scattering. The chance of multiple scattering giving rise to effect 1 must be very small.

The effect 2 must result either from a small-angle scattering or from a multiple scattering. When the measurement is made in an arrangement shown in Fig. 1, the probability of the latter is negligible. A photon scattered with a small change of direction (e.g. a few degree), $\theta$, loses so small an amount of energy that it is hardly ever distinguished from the unscattered photon. The following familiar equation elucidates such a relationship[7]

$$h\nu = \frac{h\nu_0}{1+(h\nu_0/mc^2)(1-\cos\theta)} \tag{5}$$

where $h\nu$ and $h\nu_0$ are respectively the energy of the photon after and before the scattering. Thus, the tailing due to effect 2 is not serious.

Complete elimination of the effect 3 is practically impossible. But when the geometrical arrangement is so adjusted as to make the photon-beam enter the center of the detector, the escape-peak is less distinct.

Thus, the main cause of the tailing should be the single Compton scattering (in the detector) of photons having much higher energies.

*Differential Method.* — Several sheets of absorber made of the same material and having the same thickness are prepared. The counting rate is measured, the number of the sheets being changed one by one. When the decrease in the counting rate caused by placing one additional sheet is plotted against the number of the sheets used, the curve is more similar to an ideally exponential than the ordinary curve.

That curve, which is tentatively called "differential absorption curve" can be formulated as follows: the ordinary absorption curve is generally expressed by

$$R = A\exp(-\Phi T) + B(T) \tag{6}$$

where $\Phi$ and $T$ are respectively the absorption coefficient and the absorber thickness and $A$ is a constant, and $B(T)$ is written as

$$B(T) = \sum_n B_n \exp[-\Phi_n T] \tag{7}$$

For simplicity, the following case is considered.

$$B(T) = B\exp[-\Phi' T] + C \tag{8}$$

That is to say, the source gives only two kinds of photon, and there is a constant back ground. Then, the difference between the counting rates measured through $n$ and $n+1$ sheets of the absorber of thickness $\Delta T$ is expressed by

$$\begin{aligned} R_n - R_{n+1} &= A\exp(-\Phi n\Delta T)[1-\exp(-\Phi\Delta T)] \\ &\quad + B\exp(-\Phi' n\Delta T)[1-\exp(-\Phi'\Delta T)] \\ &= [1-\exp(-\Phi\Delta T)]\left[A\exp(-\Phi T)\right. \\ &\quad \left. + \frac{1-\exp(-\Phi'\Delta T)}{1-\exp(-\Phi\Delta T)} B\exp(-\Phi' T)\right] \end{aligned} \tag{9}$$

where $T = n\Delta T$. Comparison of Eq. 9 with Eq. 6 shows that the effect of a photon of a higher energy is reduced with the aid of the differential curve by a factor of $[1-\exp(-\Phi'\Delta T)]/[1-\exp(-\Phi\Delta T)]$. With an infinite number of

6) e. g. Ref. 1, p. 319.
7) e. g. ibid., p. 318.

infinitely thin absorbers this factor becomes $\Phi'/\Phi$, the ratio of the absorption coefficient for the photon of the higher energy to that for the lower energy. This ratio must be much less than unity. Because, as mentioned above, the energies of the two photons should differ largely from each other, and the absorption, at least for the photon of the lower energy, is mostly due to photoelectric effect. This is why the differential absorption curve is superior to the ordinary absorption curve. Such a consideration also holds in an actual case, where the source gives more photons of varying energies than shown in Eq. 8. When the counts taken are large enough in each measurement with varying numbers of the absorber sheet, the secondary differential absorption curve offers a still better result.

The differential absorption curves of $^{204}$Tl and Hg-β with copper are shown in Fig. 4. For other kinds of source and absorber material a similar improvement is observed.

*Auxiliary Absorber Method.*—For the measurement of the differential absorption curve, several sheets of the same absorber material having the same thickness are required. Practically, this requirement is hardly fulfilled. The "auxiliary absorber method" finds more general use. A thin foil of a certain material (auxiliary absorber) having as large an absorption coefficient as possible specifically for the photon in question is placed in the path of the photon-beam. Further, the decrease in the counting rate caused by this absorber is measured both in the presence and the absence of the sample. When the decrease in counting rate in the presence of the sample is divided by that in its absence, the quotient gives a fairly accurate transmittance (denoted by fraction and not by percentage) of the photon through the sample. This is true even when the absorbance of the sample is considerably great. This can be explained by the following equations. (Subscript A indicates figures for auxiliary absorber.)

$$R(T)=A\exp(-\Phi T)+B(T)$$
$$R(0)=A+B(0)$$
$$R(T_A)=A\exp(-\Phi_A T_A)+B(T_A)$$
$$R(T+T_A)=A\exp(-\Phi T-\Phi_A T_A)+B(T+T_A)$$

Hence, the quotient $D$ becomes

$$D=\frac{R(T)-R(T+T_A)}{R(0)-R(T_A)}=\frac{\left(\begin{array}{c}A\exp(-\Phi T)[1-\exp(-\Phi_A T_A)]\\+B(T)-B(T+T_A)\end{array}\right)}{A[1-\exp(-\Phi_A T_A)]+B(0)-B(T_A)} \quad (10)$$

When

$$\left.\begin{array}{l}B(0)=B(T_A)\text{ and }B(T)=B(T+T_A)\\D=\exp(-\Phi T)\end{array}\right\} \quad (11)$$

The larger the $\Phi_A$ is and the smaller the $T_A$ is, the better are satisfied the assumptions in Eq. 11. It is clear from a similar argument given in the "differential absorption method" that the auxiliary absorber method offers an improved absorption curve. This curve is also always superior to the differential absorption curve. The differential method can be regarded as a special case of the auxiliary absorber method, each of the absorbers in the former being itself the auxiliary absorber in the latter.

Absorption curves of a solution of barium chloride (0.114 g./ml.) in dilute hydrochloric acid are shown in Fig. 5 with the absorption curve of hydrochloric acid containing the same quantity of chlorine. The auxiliary absorber is a thin tin foil, through which about 53% of photons transmit.

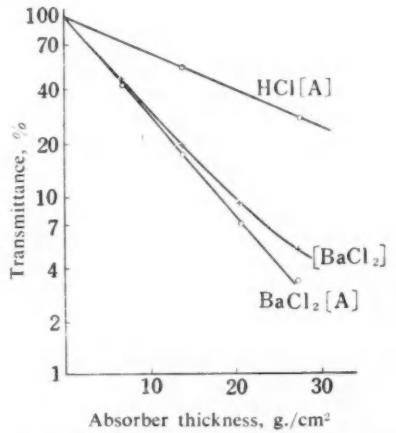



Fig. 5. Absorption curves. $BaCl_2$ [A] and HCl [A] are the auxiliary absorption curves. [$BaCl_2$] is the ordinary absorption curve.

**Effect of Geometrical Arrangement.**—A change of apparent absorption coefficient is clearly observed for an absorber having a small absorption coefficient according to the geometrical arrangement. For such an example, absorption curves of polystyrene for the photon from $^{204}$Tl are shown in Fig. 4. The curve denoted by [X] means that the absorber is placed as shown in Fig. 1, and the one denoted by [Y] means that it is placed on the scintillator. When a detector, an absorber and a source are placed close to one another, the apparent absorption coeffieient is small, and

increases toward a definite value with the increase in the distances between the source and the absorber and between the absorber and the detector.

This effect is attributable to the small-angle Compton scattering with a negligible energy loss. With such an absorber, the photolectric effect and the coherent scatterings contribute only slightly, and the absorption is caused almost entirely by the Compton scattering. However, the addition of the correction value, which can be obtained from the theoretical result[8], offers a definite value independent of the geometrical arrangement, unless the source, absorber and detector are close to one another. Such a corrected value is thought to be the true absorption coefficient. For the geometrical arrangement shown in Fig. 1, the correction value to be added is 0.007 $cm^2/g$. for atoms in the absorber having an equal number of protons and neutrons. This value is about 1/20 of the total Compton-scattering cross section of the atom for a photon of 100 keV. Thus, this correction value can be used for all kinds of absorber material and for all kinds of photon-beam with quite a little final fractional error, so far as the absorption is mainly due to the photoelectric effect.

**Relationship between the Absorption Coefficient and the Photon Energy.** — Fairly good absorption curves and accurate absorption coefficients are obtained with the aid of techniques described above. The total cross section of the Compton scattering by an electron is almost independent of the binding state. The relationship between the total cross section of the Compton scattering and the photon energy is found in various literatures.

Amidst the coherent scatterings of photons[9] with which we are concerned here, only the Rayleigh scattering has a significant contributions, though its cross section is much smaller than that of the photoelectric absorption. The dependence of Rayleigh-scattering cross section on the photon energy is not greatly different from that of the photoelectric effect.

Thus, $\phi$, the absorption coefficient excluding the contribution of the Compton scattering is proportional to $E^{-\lambda}$, or,

$$\phi = kE^{-\lambda} \qquad (13)$$

where $8/3 < \lambda < 7/2$, and $k$ is a constant.

The experimental results shown in Fig. 6 agree with Eq. 13. They agree also with other absorber materials such as tungsten, neodymium, barium, iodine and aluminum. These experimental results indicate that Eq. 13 is valid not only above but also under the K-absorption edge, with a change of the magnitude of $k$ at the edge. This relationship plays an important role in further extension of the present study. However, it is doubtful, whether an extrapolation of a curve in Fig. 6 to a region of much lower energy (e.g. $^{55}Fe$ as the source) provides a correct value.

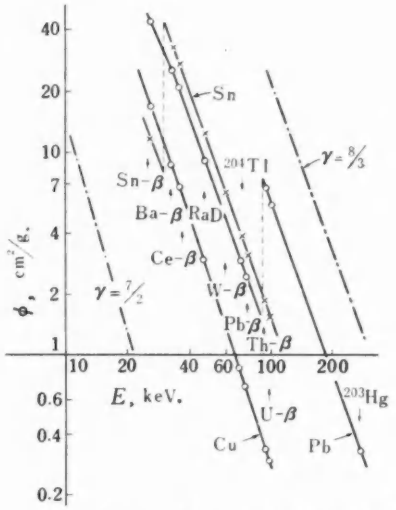



Fig. 6. Relationship between Absorption coefficient and photon energy.

There are numerical tables and charts calculated theoretically for the absorption coefficient against the photon energy. The value, however, is not entirely trustworthy for a photon having an energy not much larger than the binding energy of an electron in the absorber material, because of the invalidity of the Born approximation[10]. For the region under the K-absorption edge, the experimental values are usually considerably larger than the theoretical.

### Experimental

**Photon-beam Source.** — A solution containing radioisotopes of high specific activity emitting useful photons together with $\beta$-rays, was dried up in a hole dug in a small piece of polystyrene block, and the hole was filled with solid paraffin. When such a radioisotope was dried up in an iron dish or kept without $\beta$-ray absorber, the absorption curve, deviated further from the exponential curve. To improve the absorption curve, a solution containing $^{204}Tl$ was dried up on a crossing of polystyrene fibers at the center of a cubic polystyrene box of 5 cm. dimension, and the air in the box was replaced by hydrogen. However, only a little improvement was observed.

8) e. g. K. Siegbahn, "Beta- and Gamma-ray Spectroscopy", North Holland Pub. Co., Amsterdam (1954), p. 33.
9) e. g. ibid., p. 528.
10) e. g. ibid., p. 857.

About 50 mc. of $^{90}Sr$ of a high specific activity was dried up on a ring-formed filter paper for use as a $\beta$-ray source of the $\beta$-ray-excited-X-ray generator. It was essential to shield the detector from scattered photons by thick lead blocks. Targets of the generator were prepared as follows. Metal plates of a suitable thickness were formed as shown in Fig. 1, for use as the target. For other materials, compounds with lighter elements, such as uranium oxide, thorium oxide, mercury(I) chloride, tungsten oxide, cerium(IV) oxide, barium carbonate and ammonium bromide were placed on polystyrene target holders to a layer of due thickness with the aid of a benzene solution of polystyrene. The polyethylene sheet covering the lead block of the generator suffered radiation damage and had to be renewed with great care within a year.

**Detector.**—A scintillator (NaI, 1"×1", Harshow) was mounted with the aid of a silicone oil on a photomultiplier tube (du Mont 6292), which was selected out of several tubes by examining their stability and thermal noise (a thinner crystal would be preferable for some cases). Heater voltage for the linear amplifier and preamplifier must be stabilized. The unit having the longest resolving time in the counter assembly was the pulse-height analyzer (5 $\mu$sec.), others having much smaller resolution time. Throughout the work, the gain of the linear amplifier and the preamplifier and the applied voltage to the photomultiplier tube were kept constant, unless a $\gamma$-ray having a higher energy than 200 keV. was measured. The scale in the abscissa of Fig. 2 was the bias voltage (base line) of the single channel analyzer under that condition. The window width for the photo-peak counting was 5.4 V. for a source of a higher energy than RaD and 3.6 V. for that of a lower energy than Ce-$\beta$ respectively under the same condition. The counting rate without absorber was about $10^4$ to $2\times10^4$ c. p. m. in other cases than $^{203}Hg$, in which the rate was about $10^5$ c. p. m.

Under the condition of the photo-peak counting, the fraction of $K\beta$ rays appearing in the measurement range was as follows (denoted by percentage); U-$\beta$ 9, Th-$\beta$ 9, Pb-$\beta$ 15, Hg-$\beta$ 17, W-$\beta$ 22, Ce-$\beta$ 33, Ba-$\beta$ 35 and Sn-$\beta$ 44. For $K\beta$-filter, barium carbonate powder and iodoform were used for Ce-$\beta$ and Ba-$\beta$ respectively, both being painted on a thin filter paper in viscous benzene solution of polystyrene.

Proportional counter tubes (1.6 cm. diameter, 10 cm. effective length) of end-window type (1.9 mg./cm$^2$ mica) filled with methane (4 cm.Hg) and xenon, krypton or a mixture of these (ca. 40 cm.Hg) were set up and their characteristics measured. The output pulse of the tube was preamplified and introduced into the same electronic devices as those used with the scintillation head. The tube was also connected to a simple G-M counter circuit.

**Absorbers and Measurement of Absorption Coefficient.**—Metal-plate absorbers of aluminum, copper, tin, molybdenum and lead were obtained commercially or by rolling the pure metal to a desired thickness. A known quantity of pure iodine was dissolved in ethanol and made up to a definite volume. Pure barium and neodymium carbonates were dissolved in hydrochloric acid of a suitable concentration, and the content of the element was determined gravimetrically. Absorption curves of both the solution and the solvent were determined, and the absorption coefficient of the element was calculated, volume change due to the dissolution being taken into account.

## Summary

Studies for the improvement of fundamental techniques for the chemical use of the absorption of soft $\gamma$-rays, $\beta$-ray-excited X-rays and K-capture X-rays were undertaken. The exponential absorption curve, which is essential for the measurement of the accurate absorption coefficient and for many quantitative works, was obtained by the use of a proper detection method and the differential absorption technique, even in the presence of some photons having various energies. The relationship between the absorption coefficient thus obtained and the photon energy proved to agree with the theoretical result.

*The Electrical Communication Laboratory*
*Musashino, Tokyo*

# *Visible Absorption Spectra of 1, 3, 5-Trinitrobenzene and its Derivatives in Aqueous Alkaline Acetone*

By Takehiro ABE

(Received January 16, 1961)

In a previous short communication[1] it was reported that when an acetone solution of 1, 3, 5-trinitrobenzene was treated with aqueous sodium hydroxide intense 460 and weak 510~590 mμ bands appeared and when ammonia water was applied an intense 505 mμ band came out. In the present work, the same spectroscopic investigation has been made on similar reactions of aqueous sodium hydroxide and of aqueous ammonia with 1, 3, 5-trinitrobenzene derivatives of 1, 3, 5-trinitrobenzene, 2, 4, 6-trinitrotoluene, tetryl (2, 4, 6-trinitrophenylmethylnitramine) and picryl chloride, in acetone.

## Expermental

Commercial extra pure grade trinitro compounds and commercial grade acetone were purified by the same methods as in the previous paper[2]. Sodium hydroxide and ammonia water (ca. 28%) of commercial grade were used without further purification.

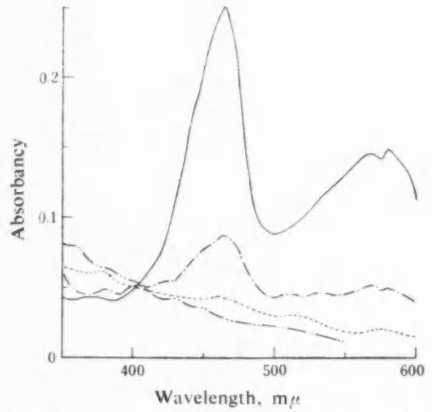



Fig. 1. Absorption spectra of 1,3,5-trinitrobenzene ($1.06\times10^{-5}$ M) in acetone (containing 4% water by volume) in the presence of sodium hydroxide ($4.16\times10^{-2}$ N) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 – – – – After 2 hr.
4 —··— After 5 hr.

Each colored solution was made pipetting 1 cc. of an aqueous alkaline solution into 1 cc. of acetone solution of each trinitro compound and diluting the resulting solutions with acetone to 25 cc. Spectra of all the colored solutions were measured, using a Hitachi EPU-2 spectrophotometer at room temperature. The length of the absorption cells was 1 cm.

## Results and Discussion

**Absorption Spectra of the Trinitro Compounds in Aqueous Acetone Containing Sodium Hydroxide (Figs. 1–4).**—When dilute aqueous solutions of sodium hydroxide are added, all the

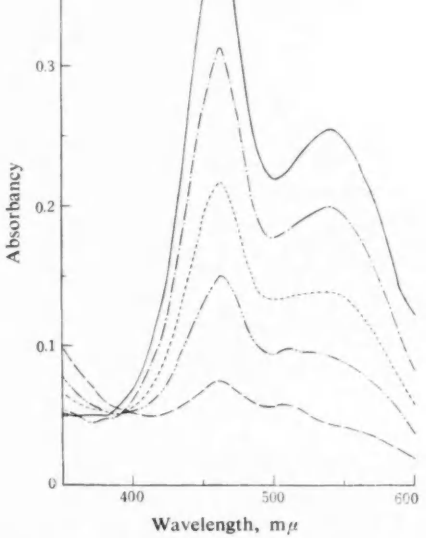



Fig. 2. Absorption spectra of 2,4,6-trinitrotoluene ($1.68\times10^{-5}$ M) in acetone (containing 4% water by volume) in the presence of sodium hydroxide ($4.16\times10^{-2}$ N) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 – – – – After 2 hr.
4 —··— After 3 hr.
5 ——— After 5 hr.

1) T. Abe, This Bulletin, 32, 778 (1959).
2) T. Abe, ibid., 32, 339 (1959).

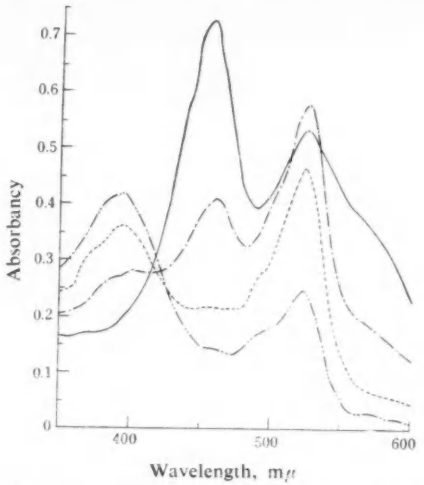



Fig. 3. Absorption spectra of tetryl ($3.95\times10^{-5}$ M) in acetone (containing 4% water by volume) in the presence of sodium hydroxide ($4.16\times10^{-2}$ N) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 2 hr.
4 —··— After 4 hr.

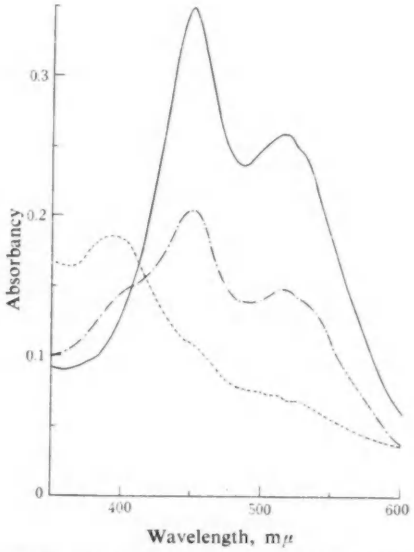



Fig. 4. Absorption spectra of picryl chloride ($1.73\times10^{-5}$ M) in acetone (containing 4% water by volume) in the presence of sodium hydroxide ($4.16\times10^{-2}$ N) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 3 hr.

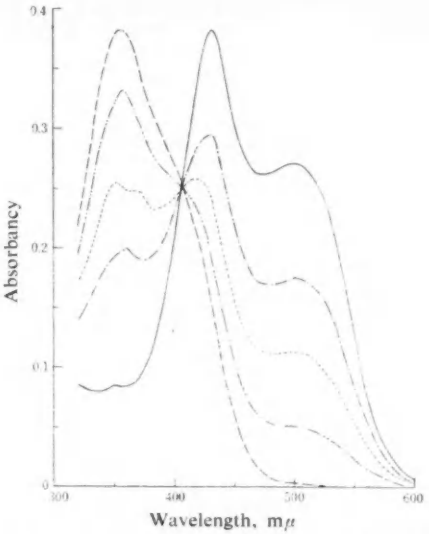
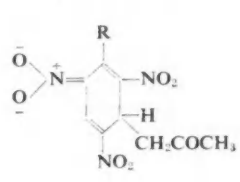


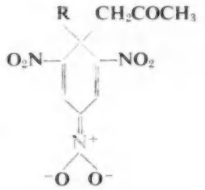

Fig. 5. Absorption spectra of tetryl in water containing sodium hydroxide at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 2 hr.
4 —··— After 4 hr.
5 ——— After a day

acetone solutions of these trinitro compounds initially show similar absorption curves 1. The analogy among the absorption curves 1 in Figs. 1–4 is not in perfect accord with Kimura's results[3]. He reported that a spectral pattern of a colored solution produced by treating trinitrobenzene with sodium hydroxide in a mixture of acetone and methanol (50% by volume) was different from patterns similarly made from trinitrotoluene and picryl chloride, and that the former was due to structure I while the latter ones were due to both structures I (mainly) and II.




I

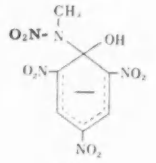



II

A change in an absorption curve of the aqueous alkali-treated colored solution of tetryl with time is indicated in Fig. 5. The colored solution made by adding a drop of aqueous

3) M. Kimura, *Pharm. Bull. (Japan)*, **3**, 75 (1955).

sodium hydroxide solution (1 N) to a dilute aqueous solution of tetryl is decolorized at the highest measurable rate at room temperature among those of the four trinitro compounds. The decolorized solution shows an absorption curve 5 similar to that of picrate anion. It is well known that tetryl reacts with aqueous alkali to form picrate. Accordingly, as mentioned in the previous paper[4], a curve in Fig. 5 is expected to be due to Meisenheimer's intermediate III in the process of substitution reaction of tetryl to picric acid.



III

Recently such Meisenheimer's intermediates have been presented for many colored products of polynitrobenzene derivatives with alkalies*. From the close similarity of the absorption curves 1 in Figs. 1–4 with that 1 in Fig. 5 it seems likely that the curves 1 in Figs. 1–4 do not correspond to products such as I or II but do to such Meisenheimer's type complexes, III, formed between the trinitro compounds and sodium hydroxide.

When the colored solutions for Figs. 1–4 are allowed to stand for several hours, they become turbid. Their spectra can not, therefore, be measured thereafter. Figs. 3 and 4 suggest that both the colored species from tetryl and picryl chloride are gradually converted into a substance giving an absorption band at about 390 mμ. Picric acid in acetone also gives an absorption band at the same region in the presence of sodium hydroxide[4]. Accordingly, the colored species from tetryl and picryl chloride in acetone as well as in water are probably converted mainly into picric acid. On the other hand, the colored solutions of trinitrobenzene and trinitrotoluene do not have distinct bands at about 390 mμ even after decoloration, as indicated in Figs. 1 and 2. Therefore, those from trinitrobenzene and trinitrotoluene would undergo further complicated reactions like the reaction of trinitrobenzene with sodium carbonate in methanol, finally giving 3,5-dinitroanisole through the formation of the Meisenheimer's intermediate[5].

**Absorption Spectra of the Trinitro Compounds in Acetone Containing Ammonia Water (Figs. 6-9).**—Figs. 6–9 show that colored solutions initially produced by additions of ammonia water to the acetone solutions of the trinitro compounds give absorption curves 1 similar to these for the colored solutions obtained by

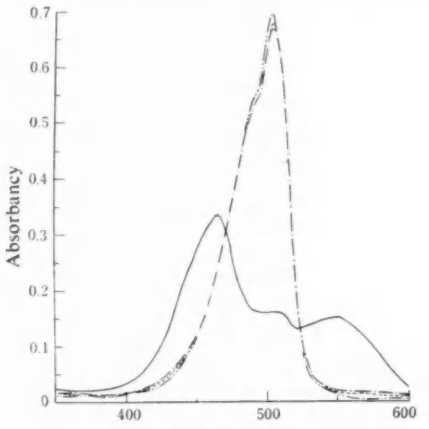



Fig. 6. Absorption spectra of 1,3,5-trinitrobenzene ($1.23\times10^{-5}$ M) in acetone (containing 4% water by volume) in the presence of ammonia (1.2%) at room temperature.

1 ——— Immediately after the preparation
2 —·—·— After 1 hr.
3 – – – – – After 3 hr.
4 —··—··— After a day

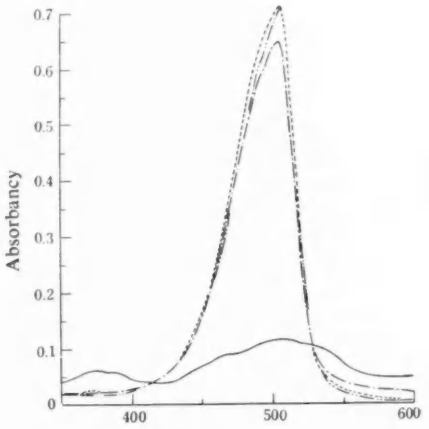



Fig. 7. Absorption spectra of 2,4,6-trinitrotoluene ($1.68\times10^{-5}$ M) in acetone (containing 4% water by volume) in the presence of ammonia (1.2%) at room temperature.

1 ——— Immediately after the preparation
2 —·—·— After 1 hr.
3 – – – – – After 3 hr.
4 —··—··— After a day

* For example, see Ref. 4.

4) T. Abe, This Bulletin, **34**, 21 (1961).
5) P. T. Izzo, *J. Org. Chem.*, **24**, 2026 (1959).

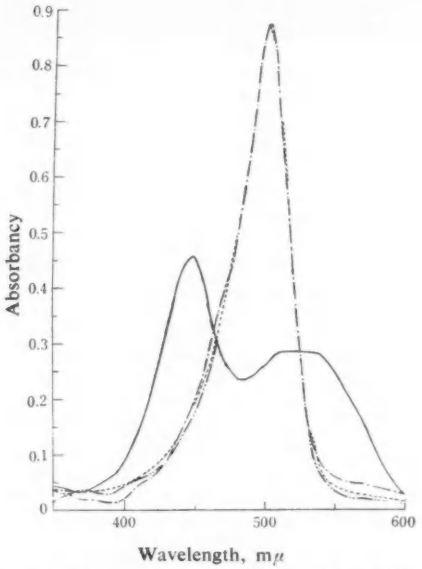



Fig. 8. Absorption spectra of tetryl ($2.00\times10^{-5}$ M) in acetone (containing 4% water by volume) in the presence of ammonia (1.2%) at room temperature.
1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 3 hr.
4 —··— After a day

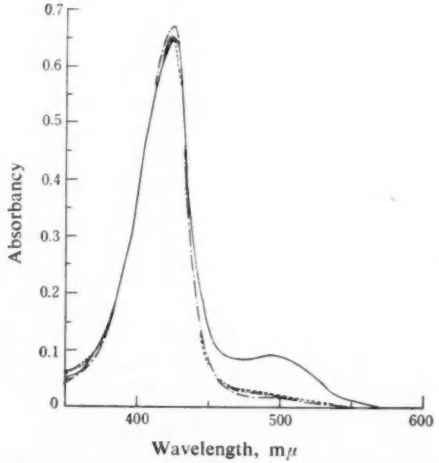



Fig. 9. Absorption spectra of picryl chloride ($1.65\times10^{-5}$ M) in acetone (containing 4% water by volume) in the presence of ammonia (1.2%) at room temperature.
1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 3 hr.
4 —··— After a day

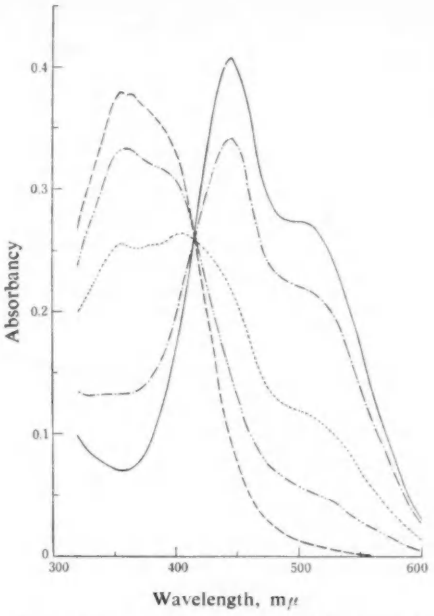



Fig. 10. Absorption spectra of tetryl in water containing ammonia at room temperature.
1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 4 hr.
4 —··— After 8 hr.
5 ——— After a day

the addition of sodium hydroxide, except in the case of the solution from trinitrotoluene, and that the initially produced colored solutions change to the other solutions having different stable intense bands. The absorption curve 1 in Fig. 7 is the only one which does not correspond to the curve 1 in Fig. 2, but does to the curve[6,7] for a colored solution formed from trinitrotoluene in ethanol by the action of sodium ethoxide. Caldin et al.[6,7] have suggested a proton-transfer reaction. Miller and Wynne-Jones[8] also observed that a mixture of trinitrobenzene with diethylamine in acetone or in ethanol produced at first an intensely colored solution having absorption maxima at 470, 515 and 570 mμ and that the solution changed after a considerable period to that having an absorption band only at 515 mμ.

One can see from Fig. 10 that both ammonia water and sodium hydroxide react identically

6) E. F. Caldin and G. Long, *Proc. Roy. Soc.*, **A228**, 263 (1955).
7) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528.
8) R. E. Miller and W. F. K. Wynne-Jones, ibid., **1959**, 2375.

with tetryl in water. From the similarity of the absorption curves 1 in Figs. 1–5 and 10, the absorption curves 1 in Figs. 6, 8 and 9 are perhaps due to the colored intermediates such as III, except for the case of trinitrotoluene. These initially formed colored intermediates may further react to produce a stable colored species giving the final absorption curves 4 in Figs. 6–9. The stable colored species were provisionally considered to be Meisenheimer's intermediates in the previous paper[9]. However, it has not yet been proved that the stable colored species are converted further into picric acid. Therefore, at present one can not conclude that they are the Meisenheimer's intermediates. Kimura[10] reported that a darkish purple substance obtained by adding sodium bicarbonate to the acetone solution of trinitrobenzene was a product similar to II.

**Summary**

The visible absorption spectra of the colored solutions produced by adding aqueous sodium hydroxide solution or ammonia water to the acetone solutions of 1, 3, 5-trinitrobenzene and its derivatives (2, 4, 6-trinitrotoluene, tetryl and picryl chloride) were measured at room temperature in order to investigate the difference of the chemical actions between stong-alkaline sodium hydroxide and weak-alkaline ammonia water.

These trinitro compounds in acetone containing sodium hydroxide show spectra similar to that of the aqueous sodium hydroxide solution of tetryl. The spectrum of this aqueous colored solution is considered to be due to an intermediate of the Meisenheimer type in the process of the substitution reaction of tetryl to picric acid. Consequently, all the spectra of the colored solutions from the trinitro componds are also probably due to the intermediates of the Meisenheimer type.

Each colored solution of the trinitro compounds in acetone containing ammonia water initially shows the same spectrum as that with sodium hydroxide, except for the case of trinitrotoluene, and changes to the other colored solution having an intense and stable band entirely different from the initial spectrum. The initially formed colored solutions of these trinitro compounds, except the solution from trinitrotoluene, may also be due to the Meisenheimer intermediates.

The author is particularly indebted to Professor Yōkan Nomura for helpful discussions.

*Department of Chemistry*
*Defense Academy*
*Yokosuka*

9) T. Abe, This Bulletin, **32**, 997 (1959).
10) M. Kimura, *J. Pharm. Soc Japan* (*Yakugaku Zasshi*), **73**, 1219 (1953).

---

# *Sur la Dissolution des Minerais Sulfurés en Divers Milieux. V. Dissolution de la Sphalérite*

Par Masami ICHIKUNI et Hiroshi KAMIYA

(Reçu le 20 Janvier 1961)

Lorsqu'on aborde le problème de la désagrégation des minerais sulfurés par voie chimique, on s'intéresse notamment aux réactions qui ont part à ce phénomène. Bien que de nombreux articles soint déjà parus à ce propos, ces études sont faites, dans la plupart des cas, avec l'utilisation des minerais et non des minéraux. L'interprétation des résultats était très difficile, car les analyses chimiques n'ont donné que l'aspect global du phénomène composé de nombreuses réactions qui s'avançaient chacune à vitesse différente. Il faut qu'on sache quelles réactions peuvent avoir lieu et ont lieu au cours de la désagrégation.

Pour l'analyse des résultats, la sphalérite semble se munir d'un caractère favorable grâce à la simplicité de sa composition chimique. Kuz'minykh et Yakhontova[1] ont déjà étudié l'extraction du zinc à partir de ce minéral en utilisant le sulfate de fer (III) comme réactif. Il s'agit de la dissolution du minéral en milieu extrêmement oxydant ; ce milieu ne représenterait pas celui de la nature. Ohashi[2] a examiné la dissolution des minéraux sulfurés dans les

1) I. N. Kuz'minykh et E. L. Yakhontova, *Zhur. Prinklad. Khim.* (*J. Applied Chem.*), **23**, 1121 (1950).
2) S. Ohashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 845 (1953).

eaux saturées d'air, mais il est regrettable que cet auteur n'ait pas montré les réactions de dissolution. Récemment, du point de vue électrochimique, Sato[3] a donné le mécanisme de la décomposition des minéraux sulfurés dans une solution choisie.

Les présents auteurs voudraient montrer les réactions de la décomposition de la sphalérite en diverses solutions et préciser les conditions qui favorisent la désagrégation, tout en tenant compte des composants mineurs en solution. Il est probable que ces derniers se chargent du rôle de catalyseur dans la nature. L'accélération des réactions est souvent due uniquement à l'action du catalyseur. On tâtonne encore quelles substances peuvent être un catalyseur dans la désagrégation des minerais sulfurés.

### Méthode d'Expérience

On suspend 500 mg. de sphalérite pulvérisée dans 200 ml. de liqueur à l'aide d'un agitateur magnétique, et effectue le prélèvement de 5 ml. de liqueur à des intervalles appropriés au cours de 2 hr. de traitement. Le ballon à fond plat à 300 ml. contenant la liqueur est plongé dans un bain-marie dont la température est maintenue constamment à 50 C. Le ballon est bien bouché avec un bouchon de caoutchouc, persé de 2 tuyaux de verre: le plus long, dont le bout de dessous se munit d'un hémisphère de verre fritté qui touche presque le fond du ballon, sert à produire de nombreuses petites bulles d'air dans la liqueur, lorsqu'on relie à une trompe le tuyau le plus court qui ne s'enfonce pas dans la liqueur. Le débit de l'air est réglé à 0,4 l./min.

La sphalérite produite à la mine de Hosokura, département de Miyagi, est pulvérisée et passée au tamis 60. Le Tableau I montre le résultat d'analyse de l'échantillon. Une certaine teneur en plomb s'explique par la présence de la galène qui est une des impuretés minéralogiques les plus communes. On a préparé ici deux échantillons en pulvérisant de nouveau de la sphalérite tamisée dans un mortier d'agate. Un échantillon qui a été utilisé pour l'examen de l'influence du pH sur la dissolution de ce minéral était moins fin que l'autre avec lequel on a effectué les autres expériences.

Tableau I. Résultat d'analyse chimique de la sphalérite

| Composant | Teneur, % |
|---|---|
| Zn | 61,78 |
| Fe | 1,29 |
| Cd | 0,38 |
| Mn | 0,06 |
| Cu | 0,01 |
| Pb | 2,62 |
| S | 31,53 |
| $SiO_2$ | 0,21 |
| Total | 97,88 |

3) M. Sato, *Econ. Geol.*, 55. 1202 (1960).

La liqueur prélevée est immédiatement filtrée et amenée à 25 ml. Sur cette solution diluée on effectue le dosage du zinc, et s'il y a lieu, du fer et du cuivre. Le dosage du zinc et du cuivre est fait par voie colorimétrique au moyen de la dithizone, et celui du fer, au moyen de l'*o*-phénanthroline. Le dosage de l'hydrogène sulfuré a été effectué par l'iodométrie après une filtration soigneuse de liqueur. L'ion sulfate est examiné avec une solution de chlorure de baryum.

### Résultats

**Effets du pH.**—Quand on a introduit de l'air, la vitesse de dissolution du zinc dépendait dans une grande mesure de l'acidité du milieu. La sphalérite s'est dissoute rapidement au début du traitement, et dont la vitesse de dissolution a ralenti graduellement et elle est devenue constante dans une demi-heure (voir la Fig. 2). Cette vitesse constante servait à établir une échelle de comparaison entre toutes les conditions des expériences.

Le résultat des expériences est indiqué sur la Fig. 1. Comme elle l'indique, la vitesse de dissolution décroit avec la diminution de l'acidité du milieu. L'ion sulfate n'a été décelé en aucun cas. On remarque donc une réaction qui suit:

$$(1) \qquad ZnS + 2H^+ \rightarrow Zn^{2+} + H_2S$$

A part de cette réaction, on en a une autre qui conduit à la formation du soufre libre:

$$(2) \quad ZnS + 2H^+ + O \rightarrow Zn^{2+} + S + H_2O$$

Comme la formation du soufre libre était négligeable, on admet que la première réaction est prédominante sous les conditions des expériences. On n'arrive pourtant pas à décider si la formation du soufre libre est attribuable à l'oxydation de l'hydrogène sulfuré, formé par la première réaction, ou à l'oxydation directe du minéral.

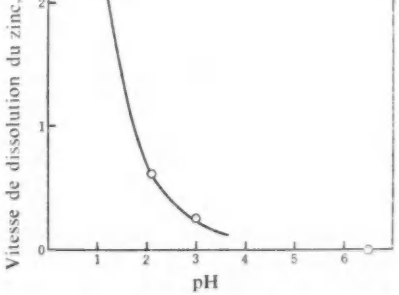



Fig. 1. Vitesse de dissolution de la sphalérite en fonction du pH (expériences effectuées avec barbotage d'air de 400 ml./min.).

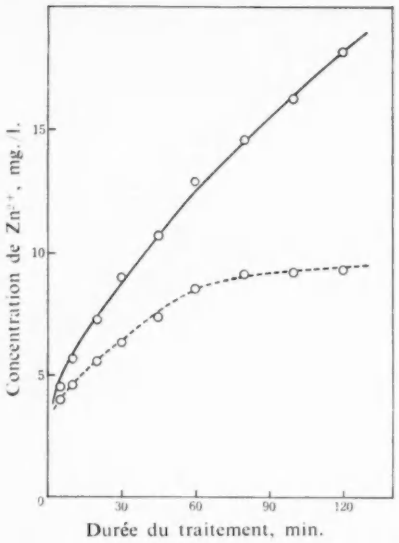



Fig. 2. Variation de concentration de $Zn^{2+}$ en fonction de la durée du traitement.
Trait plein : expérience effectuée avec l'introduction de l'air
Trait discontinu : expérience effectuée sans introduction de l'air

Il faut qu'on tienne compte de la granulométrie de l'échantillon utilisé dans cette expérience, lorsqu'on compare ce résultat avec celui des expériences exposées ci-après qui ont été effectuées avec l'échantillon plus fin.

**Effets du Barbotage de l'Air.**—Il faut qu'on sache d'abord si l'oxygène barboté agit en oxydant du minéral et de l'hydrogène sulfuré, ou simplement en entraîneur de celui-ci. A cet effet, deux expériences ont été entreprises: l'une, avec l'introduction de l'air, dont le débit était de 0,4 l./min., et l'autre, sans introduction de l'air. Dans la dernière expérience, l'air ne se comportait pas en entraîneur, et cela ne signifie pas l'expulsion entière de l'oxygène. Les deux ont été effectuées en milieu d'acide chlorhydrique 0,01 N et à la température de 50°C. Dans la Fig. 2, on dessine la concentration de zinc en fonction de la durée du traitement. Comme on voit dedans, deux courbes, correspondant chacune aux deux expériences décrites ci-dessus, s'approchent l'une de l'autre au début de la dissolution, cependant, elles s'éloignent rapidement avec le temps. La différence des deux expériences peut s'expliquer par l'accumulation de l'hydrogène sulfuré. Cette supposition sera très compréhensible, si l'on admet que le barbotage de l'air, entraînant avec celui-ci l'hydrogène sulfuré formé, favorise une dissolution remarquable du minéral. En fait, sans introduction de l'air, la teneur en hydrogène sulfuré a atteint une valeur de 2,1 mg./l. au bout de 2 hr. de traitement.

Examinons ensuite la possibilité de l'oxydation de l'hydrogène sulfuré par l'oxygène dissous. Si la réaction d'oxydation de ce composé s'avançait avec une vitesse considérable, l'empêchement de la dissolution n'aurait pas lieu, tout au moins, pendant un certain temps, car la liqueur contenait 5,0 mg./l. d'oxygène dissous avant l'addition du minéral. Au bout de 2 hr. de traitement, on a trouvé une concentration de zinc de 9,3 mg./l., correspondant à la formation de l'hydrogène sulfuré de 4,8 mg./l. Ce chiffre ne suffit pas à consumer entièrement l'oxygène dissous, même si l'hydrogène sulfuré soit complètement oxydé en soufre libre par l'oxygène contenu dans la liqueur. D'ailleurs la surface de la liqueur étant toujours en contact avec l'atmosphère, il n'y a aucune raison de croire que l'accumulation de l'hydrogène sulfuré a été causée par manque d'oxygène libre.

Par suite de ces considérations, on conclut que l'oxydation de l'hydrogène sulfuré par l'oxygène libre s'avance très lentement, et que l'hydrogène sulfuré ralentit la décomposition de la sphalérite, même en présence de l'oxygène atmosphérique. Il va sans dire qu'à l'état d'équilibre, la présence de l'hydrogène sulfuré n'est pas compatible avec celle de l'oxygène libre. Le système réalisé par les expériences était hors de l'équilibre, comme l'indique la co-présence de l'hydrogène sulfuré et de l'oxygène. La théorie de l'équilibre chimique ne sera pas très utile à expliquer le mécanisme des réactions qui ont lieu au cours du traitement.

Calculons ici le produit de concentration de zinc par celle d'ion sulfure avec les chiffres qu'on a obtenus sur l'expérience effectuée sans introduction de l'air, au bout de 2 hr. de traitement :

$$[Zn^{2+}] = 9{,}3 \text{ mg./l.} = 1{,}4 \times 10^{-4} \text{ mol./l.}$$

$$[H_2S] = 2{,}1 \text{ mg./l.} = 0{,}62 \times 10^{-4} \text{ mol./l.}$$

Comme $[H^+]^2[S^{2-}]/[H_2S] = 10^{-21}$, où $[H^+] = 10^{-2}$, on a :

$$[S^{2-}] = 0{,}62 \times 10^{-21} \text{ mol./l.}$$

donc,

$$[Zn^{2+}] \cdot [S^{2-}] = 0{,}87 \times 10^{-25}$$

Cette valeur est beaucoup moins grande que le produit de solubilité de la sphalérite : $10^{-23{,}3}$. On notera ici que la vitesse de dissolution du minéral est déjà très ralentie sous cette condition.

**Effets des Ions $Fe^{2+}$.**—Cet essai s'est fait à 50°C, en milieu d'acide chlorhydrique 0,01 N, avec l'introduction de l'air dont le débit était de 0,4 l./min. On a préparé une solution

étalon de $Fe^{2+}$ en dissolvant du chlorure de fer(II) hydraté dans l'acide chlorhydrique 0,01 N. Elle contenait 1,000 mg./l. de $Fe^{2+}$.

Les ions $Fe^{3+}$ exercent une action particulière sur la dissolution du minerai sulfuré, dans ce cas ils se réduisent en ions $Fe^{2+}$. Une solution qui est en contact avec un gisement de minerais sulfurés trouve son fer presque entièrement à l'état divalent. Les ions $Fe^{3+}$ se forment dans la nature par l'oxydation des ions $Fe^{2+}$ au moyen de l'oxygène atmosphérique. On a effectué ces expériences en prenant le mécanisme de la formation des ions $Fe^{3+}$ dans la nature en considération. Par l'introduction de l'air dans une solution contenant des ions $Fe^{2+}$, on a essayé de reproduire en quelque sorte la formation des ions $Fe^{3+}$. On avait déjà noté que l'action des ions $Fe^{2+}$ et de l'oxygène atmosphérique favorisait une forte dissolution de la chalcopyrite, et on l'avait attribué à la formation des ions $Fe^{3+}$ [4].

On montre sur la Fig. 3 un exemple tiré des expériences: la présence des ions $Fe^{2+}$ ralentit considérablement la dissolution du zinc. Même une teneur en ions $Fe^{2+}$ à 100 mg./l. produit le même effet, comme on voit sur la Fig. 4. Lorsqu'on dit vitesse de dissolution, il s'agit toujours de celle qui est mesurée à l'état stationnaire de dissolution. Ce résultat ne s'accorde pas avec celui de la chalcopyrite.

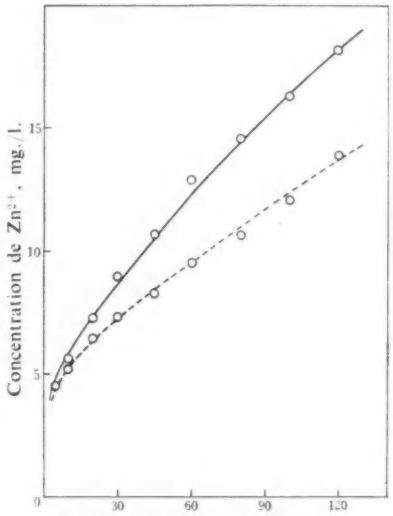



Fig. 3. Variation de concentration de $Zn^{2+}$ en fonction de la durée du traitement.
Trait plein: en l'absence des ions $Fe^{2+}$
Trait discontinu: en présence de 1.000 mg./l. de $Fe^{2+}$

4) M. Ichikuni, Ce Bulletin, 33, 1159 (1960).

**Effets des Ions $Fe^{3+}$.**—Cet essai a été effectué à 50°C, en milieu d'acide chlorhydrique 0,01 N, avec l'introduction de l'air, dont le débit restait toujours le même que les essais précédents. La solution étalon de $Fe^{3+}$ a été préparée à partir du chlorure de fer(III) hydraté. On en a dissous dans l'acide chlorhydrique, de manière à ce que la solution contienne 100 mg./l. de $Fe^{3+}$.

La réaction entre la sphalérite et des ions $Fe^{3+}$ est exprimée par l'équation suivante[1]:

$$(3)\quad ZnS + 2Fe^{3+} \rightarrow Zn^{2+} + S + 2Fe^{2+}$$

où la dissolution de 1 mol. de zinc correspond à la réduction de 2 mol. de $Fe^{3+}$ en $Fe^{2+}$. L'examen du résultat d'expériences, montré

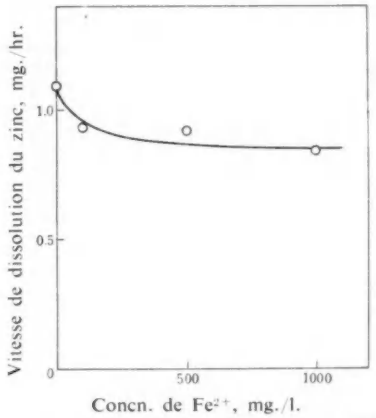



Fig. 4. Vitesse de dissolution de la sphalérite en fonction de la concentration en ions $Fe^{2+}$ de la liqueur.

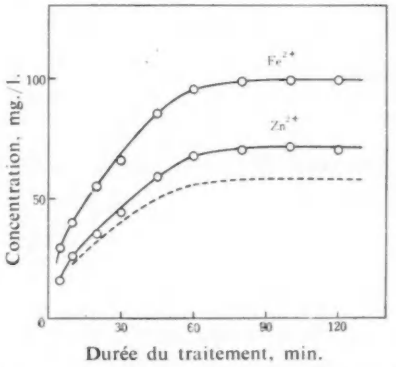



Fig. 5. Dissolution de la sphalérite par l'action des ions $Fe^{3+}$.
Trait plein: concentration de zinc dissous et defer réduit
Trait discontinu: concentration théorique de zinc, calculée à partir de la concentration trouvée de $Fe^{2+}$

sur la Fig. 5, révèle que la quantité dissoute de zinc est toujours supérieure à la quantité théorique de zinc, calculée d'après la réaction 3 à partir de la quantité trouvée de $Fe^{2+}$. Il est certain qu'une partie de zinc a été dissoute d'après la réaction 1, où l'hydrogène sulfuré a été partiellement entraîné par le courant d'air, sans être oxydé en soufre libre par l'action des ions $Fe^{3+}$.

**Effets des Ions $Cu^{2+}$.**—Il est bien connu que les ions de métaux lourds, notamment $Cu^{2+}$, jouent un rôle de catalyseur dans de diverses réactions. Comme les ions $Cu^{2+}$ se trouvent très fréquemment dans les eaux de mine, il est probable qu'ils contribuent d'une certaine manière à l'accélération ou à la retardation des réactions de désagrégation.

Bien que l'action des ions $Cu^{2+}$ ait été remarquée par certains chercheurs[5], la connaissance en est encore peu suffisante. Le comportement des ions $Cu^{2+}$ trouvé dans cette expérience permettra de révéler la fonction qu'ils exercent dans la désagrégation. Cet essai a été effectué sous les mêmes conditions que les précédents, sauf la présence des ions $Cu^{2+}$ qui ont été ajoutés saus forme du sulfate.

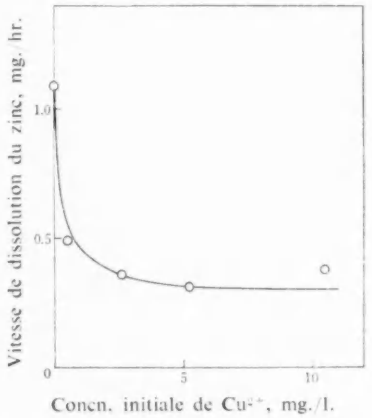



Fig. 6. Influence des ions $Cu^{2+}$ sur la dissolution de la sphalérite.

La vitesse de dissolution du zinc a été mesurée dans des solutions de diverses teneurs en $Cu^{2+}$. La Fig. 6 représente le résultat de l'essai. Les ions $Cu^{2+}$ ralentissent la dissolution. Une variation faible de concentration en $Cu^{2+}$ révélé qu'une petite portion de $Cu^{2+}$ avait disparu au cours de l'expérience. La diminution en a atteint 0,5 mg./l. près au bout de 2 hr. de traitement. Le cuivre aurait précipité sous forme du sulfure, dont la formation est attribuable au dégagement de l'hydrogène sulfuré, libéré par la décomposition du minéral. Toutefois la quantité fixée de cuivre était très faible par rapport à celle d'hydrogène sulfuré formé. On peut en déduire que la condition oxydante défavorise la fixation du cuivre, même en présence des ions sulfure. Comme le cuivre ajouté restait presque entièrement à l'état dissous, on admet qu'une réaction d'échange du zinc avec le cuivre n'avait pas lieu. Si la réaction d'échange intervenait, il y aurait une tendance d'augmenter la vitesse de dissolution à mesure que la concentration en $Cu^{2+}$ augmente.

Or, généralement dit, des solutions formées dans la zone d'oxydation du gisement des minerais sulfurés contiennent encore d'autres ions que les ions $Cu^{2+}$. La caractéristique des solution est donc la co-présence de divers ions, tels que des ions $Fe^{2+}$, $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ et ainsi de suite. L'action des ions $Cu^{2+}$ devrait être examinée en présence d'autres ions, notamment des ions de fer.

**Effets des Ions $Fe^{3+}$ et $Cu^{2+}$.**—Il est bien connu que les ions $Fe^{3+}$ sont efficaces à la décomposition des minerais sulfurés, mais il n'y a presque aucune étude sur la contribution des ions $Cu^{2+}$ à ce phénomène. Seulement Garrels et Thompson[6] ont mentionné que l'attaque des ions $Fe^{3+}$ contre la pyrite n'était pas accélérée par la présence des ions $Cu^{2+}$. On a entrepris ici un essai de dissolution de la sphalérite au moyen des ions $Fe^{3+}$ en présence des ions $Cu^{2+}$, et en a comparé le résultat avec celui de l'essai précédent qu'on avait effectué

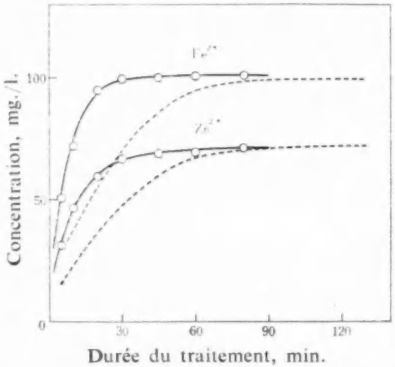



Fig. 7. Effets des ions $Cu^{2+}$ sur la dissolution de la sphalérite par l'action des ions $Fe^{3+}$.
Trait plein : expérience effectuée en présence de 5,25 mg./l. de $Cu^{2+}$
Trait discontinu : expérience effectuée en l'absence des ions $Cu^{2+}$

5) S. Koch et Gy. Grasselly, *Acta Univ. Szegediensis, Acta Mineral. Petrog.*, **6**, 23 (1952).

6) R. M. Garrels et M. E. Thompson, *Am. J. Sci.*, **258 A**, 57 (1960).

dans une liqueur contenant 100 mg./l. de $Fe^{3+}$, mais qui était exempte de cuivre.

La Fig. 7 donne les résultats de cet essai et du précédent. On voit que la présence des ions $Cu^{2+}$ favorise une décomposition rapide de la sphalérite. On ajoute encore que la diminution de concentration en $Cu^{2+}$ n'avait pas lieu au cours du traitement, tant que les ions $Fe^{2+}$ restaient en solution.

**Effets des Ions $Fe^{2+}$ et $Cu^{2+}$.**—Les résultats des essais précédents nous ont conduit à l'entreprise d'un autre essai mis sous les conditions qui ne sont das trop éloignées de celles de la nature. En considérant les eaux de mine, où les ions $Fe^{2+}$ sont prédominants dans la plupart des cas, on a imaginé que l'essai de la dissolution en présence des ions $Fe^{2+}$ et $Cu^{2+}$ réaliserait les réactions réelles dans la nature.

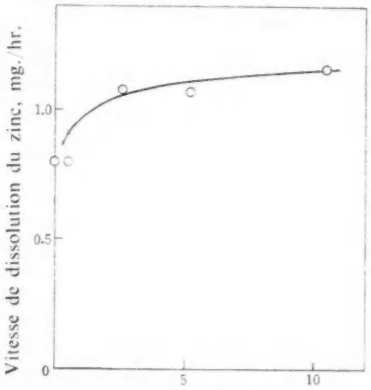



Fig. 8. Vitesse de dissolution de la sphalérite en présence de 700 mg./l. de $Fe^{2+}$ et de quantité variable de $Cu^{2+}$.

La Fig. 8 montre le résultat. Dans cette série d'expériences, la concentration de $Fe^{2+}$ était fixée à 700 mg./l. et celle de $Cu^{2+}$ variait de 0,53 à 10,5 mg./l. La concentration de $Cu^{2+}$ a diminué très lentement au cours du traitement. La diminution s'en est élevée à 0,5 mg./l. près au bout de 2 hr. de traitement. Toutefois on a remarqué une dissolution accélérée de la sphalérite, tant que l'ion cuivre restait en solution. On discutera plus loin le mécanisme possible de ce phénomène.

## Discussion

C'est le pH du milieu qui exerce une grande influence sur la décomposition du minéral, sans qu'on tienne compte des effets électrochimiques provenant du contact avec d'autres minéraux. Si le minéral existait indépendamment d'autres minéraux, il resterait assez stable en milieu neutre même en présence de l'oxygène atmosphérique.

La présence de l'oxygène libre et des ions $Fe^{2+}$ n'est pas capable d'accélérer sa décomposition, c'est que l'oxydation des ions $Fe^{2+}$ en ions $Fe^{3+}$ s'avance très lentement avec l'oxygène libre. Si les ions $Fe^{3+}$ étaient formés rapidement à partir des ions $Fe^{2+}$ par l'action de l'oxygène, l'introduction de l'air rendrait la décomposition du minéral d'autant plus facile que la teneur en ions $Fe^{2+}$ de la liqueur est plus grande.

Les ions $Cu^{2+}$, agissant souvent en catalyseur, ne sont pas tous seuls capables d'augmenter la vitesse de décomposition du minéral, par conséquent on ne peut pas attendre une réaction d'échange du zinc avec le cuivre. Il est intéressant que les ions $Fe^{2+}$ ainsi que les ions $Cu^{2+}$, loin d'accélérer la désagrégation de la sphalérite, la retardent considérablement. Ce phénomène offre des problèmes importants à la géochimie des gisements métallifères.

L'action des ions $Fe^{3+}$ avait été bien étudiée, mais on a trouvé ici, pour la première fois, qu'une petite quantité de cuivre accélérait la réaction entre le minéral et les ions $Fe^{3+}$. Toutefois les produits de réaction étaient toujours les ions $Zn^{2+}$ et le soufre libre en milieu acide, indépendamment de la présence du cuivre. On considère pour le moment le cuivre comme catalyseur.

On a eu ainsi l'idée d'examiner la dissolution du minéral en présence des ions $Fe^{2+}$ et $Cu^{2+}$ avec l'introduction de l'air. Si ces ions se comportaient indépendamment les uns des autres, ils en retarderaient la dissolution. Mais, au contraire, leur co-présence y était efficace. Ce fait insiste qu'il y a une interaction entre les ions $Fe^{2+}$, $Cu^{2+}$ et l'oxygène. Il est probable que les ions $Cu^{2+}$ facilite l'oxydation des ions $Fe^{2+}$ en ions $Fe^{3+}$ par l'oxygène atmosphérique. Ils accélèrent également l'attaque des ions $Fe^{3+}$ contre le minéral.

On conclut donc que la présence des ions $Cu^{2+}$ est indispensable à une décomposition rapide de la sphalérite, et que les ions $Cu^{2+}$ jouent ici un rôle de catalyseur. Toutefois des composés insolubles de cuivre n'en sont pas capables. On ajoute encore que, malgré l'action catalytique du cuivre, une formation abondante d'ions $Fe^{3+}$ n'aura pas lieu, le rapport $Fe^{3+}/Fe^{2+}$ étant réglé par le potentiel d'oxydo-réduction du milieu, par conséquent on ne peut pas attendre une dissolution rapide du minéral, tant que les réactions se passent en solution.

## Résumé

Les facteurs intervenant à la décomposition chimique de la sphalérite ont été examinés. Un petit pH ainsi que l'oxydant, notamment le

fer trivalent accélèrent la décomposition. La présence de l'hydrogène sulfuré la retarde considérablement. A pH 2, celle des ions $Fe^{2+}$ ou des ions $Cu^{2+}$ empêche une dissolution rapide du minéral, même avec l'introduction de l'air. La décomposition du minéral par les ions $Fe^{3+}$ est accélérée par les ions $Cu^{2+}$. La co-présence des ions $Fe^{2+}$ et $Cu^{2+}$ favorise, avec le barbotage de l'air, une dissolution remarquable du minéral, ce qui est attribuable à l'action catalytique des ions $Cu^{2+}$ qui facilitent probablement l'oxydation des ions $Fe^{2+}$ en ions $Fe^{3+}$, et l'attaque de ceux-ci contre le minéral.

Les auteurs se permettent d'exprimer leur remerciements sincères à Monsieur le professeur K. Noguchi et à Monsieur le professeur T. Hanya qui ont bien voulu donner des conseils utiles et participer à la discussion sur l'interprétation des résultats.

*Faculté des Sciences*
*Université Métropolitaine de Tokyo*
*Sétagaya-ku, Tokyo*

# *Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. I. Preparation of Cobalt Soap by Metathesis*

By Hirotaro KAMBE*

(Received February 24, 1961)

Heavy metal salts of higher fatty acids, usually called heavy metal soaps, can be made by a substitution reaction between fatty acid and the salt of weak inorganic acid such as acetate. In place of inorganic salts, oxide or hydroxide may be used. These reactions can be accelerated by fusing the reactants. This is the principle of the fusion method, which is commonly used as a means of preparation of heavy metal soaps.

Cobalt soap may be prepared by the fusion method. The melting of fatty acid with cobalt(II) acetate or cobalt(II) hydroxide is followed by the reactions:

$$Co(CH_3COO)_2 + 2RCOOH = Co(RCOO)_2 + 2CH_3COOH$$

or $$Co(OH)_2 + 2RCOOH = Co(RCOO)_2 + 2H_2O$$

The cobalt soap made by the fusion method is not crystalline powder, but a glassy mass. Molten cobalt soap is easily oxidized and often becomes dark on prolonged heating in air. For these reasons we have concluded that the fusion method is not suited for preparing pure cobalt soap.

With water soluble salts of weak acid, fatty acid may react in solution. Kaufman and Lüssling[1] reported that when they shook a solution of fatty acid in petroleum ether with an aqueous solution of cobalt(II) acetate, the upper petroleum ether layer became blue as the formed cobalt soap dissolved into petroleum ether. They obtained cobalt oleate by this method. But our preliminary experiment has shown that it is difficult to prepare cobalt stearate with this technique, for the stearate is less soluble in petroleum ether than the oleate. When we use ethyl alcohol instead of petroleum ether as the solvent, the reaction advances very smoothly in a homogeneous solution and crystalline cobalt stearate powder can be prepared. This may be another means of preparing cobalt soap, as is shown later.

Water soluble inorganic salts, either of weak acid or of strong acid, react instantaneously with alkaline soap. This type of reaction is called double decomposition or metathesis. Metathesis is most important in preparing metal soaps, and it is the basis of the so-called precipitation method. The soaps made by metathesis are generally crystalline powder.

In the case of cobalt soap, cobalt(II) chloride, nitrate, sulfate, and acetate may be used as inorganic salts in metathesis. Reactions between these and sodium or potassium soap would proceed readily in solution to form cobalt soaps. For example,

$$CoCl_2 + 2RCOONa = Co(RCOO)_2 + 2NaCl$$

Kahlenberg[2] has shown very long ago that metathetic formation of heavy metal soaps

* Present address: Aeronautical Research Institute, the University of Tokyo, Meguro-ku, Tokyo.

1) H. P. Kaufmann and Th. Lüssling, *Fette und Seifen*, 55, 90 (1953).

2) L. Kahlenberg, *J. Phys. Chem.*, 6, 6 (1902).

could be carried out also in organic solvents. Koenig[3] prepared many metal soaps, including cobalt soap, by metathesis in warm water. The soap thus formed was dried in an air oven at 115~120°C for 10~12 hr., and the glassy solid obtained was then pulverized. Koenig observed a color change from pink to blue when cobalt soap was heated.

In Koenig's method an aqueous solution of sodium soap is used, and at the lower concentrations, alkaline soap may be hydrolyzed to free acid, which will contaminate the soap being formed. Whitmore and Lauro[4] proposed a method for preventing the hydrolysis of alkaline soap by the addition of ethanol to the solution.

Although Whitmore and Lauro did not prepare cobalt soap in this way, we have examined this method in detail and found that besides common pink hydrous cobalt soap, blue anhydrous and red hydrous soaps may be formed according to conditions. In this part of the study, metathetic preparation of cobalt soap was investigated, and particularly the effects of several factors on the color of the soap being formed were discussed.

## Experimental

**Materials.**—*Fatty Acids.*—Stearic, palmitic, myristic, and lauric acid were fractionally distilled products, made by Nihon Yushi Co., and were recrystallized from absolute ethanol.

*Solvents.*—Ethanol and methanol were dehydrated and distilled over anhydrous calcium oxide. Acetone was dehydrated by potassium carbonate anhydrate.

*Cobalt(II) Salts.*—Cobalt chloride, $CoCl_2 \cdot 6H_2O$, nitrate, $Co(NO_3)_2 \cdot 6H_2O$, sulfate, $CoSO_4 \cdot 7H_2O$, and acetate, $Co(CH_3COO)_2 \cdot 4H_2O$ were chemically pure reagents and were recrystallized from water. These salts, except sulfate, are very deliquescent, and they were used with some water.

**Metathesis.**—The following standard procedure was adopted to control experimental factors.

(i) Fatty acid, mostly stearic acid, was dissolved in absolute ethanol by warming in a constant temperature water-bath at 60°C, and neutralized exactly by an alkaline solution, with phenolphthalein as indicator. The alkaline solution used was usually 0.15 N potassium hydroxide solution in water or in ethanol. If necessary, some amount of either solvent was added to the alkaline soap solution to control the ratio of the volume of solvent (ethanol in this case) to that of water in the system; this is called the solvent ratio hereafter. When this ratio is comparatively low, the alkaline soap solution becomes turbid by hydrolysis of the soap. In such cases the reaction products tend to contain free fatty acid, which may be extracted, however, by acetone, as is shown below.

(ii) An excess of cobalt salt, mostly cobalt chloride, was dissolved in the same water-bath in water, or, if necessary, in pure or aqueous ethanol. The solution of cobalt chloride in water is considerably acidic, and also the solution after metathesis becomes slightly acidic. It is natural for the soap made in this way to contain some free fatty acid. When cobalt acetate is used instead of chloride, the solution is not so acidic that free acid is not included in the soap, as was pointed out by Whitmore and Lauro[4].

(iii) After both solutions were warmed to 60°C, a cobalt salt solution was stirred into the alkaline soap solution little by little. As cobalt soap is almost insoluble in the solution, it precipitated immediately. The reaction must be carried out always below 60°C, because above this temperature the reaction products become somewhat bluish.

The color of soap in the solution was observed directly after the reaction and also after having been left in the solution for some time with or without stirring. The alkaline soap solution, which had at first shown a pink color due to phenolphthalein, became blue after the addition of a little of the cobalt salt solution because cobalt ion shows a blue color in ethanol. When the whole salt solution was added, the color of the solution faded generally, and pink soap precipitated.

(iv) The precipitates were filtered off by suction, washed by absolute ethanol to remove free fatty acid, and dried overnight in a vacuum desiccator over calcium chloride anhydrate at room temperature. The color of the soap was preserved during drying in this way. The dried soaps were pulverized by an agate mortar. Free fatty acid was extracted with acetone over anhydrous potassium carbonate in a Soxhlet extractor.

## Results and Discussion

As a preliminary experiment, the colors of cobalt soaps formed at various solvent ratios, based on volume, were observed in the solution without stirring.

In pure ethanol, the yield of cobalt soap was very little. As metathesis is an ionic reaction, it is natural that the reaction is suppressed in a solvent, in which degrees of ionization of reactants are low. A solution of cobalt chloride in pure ethanol is blue, and metathesis in this solvent proceeded in a blue solution. But the reaction product was not pure blue; it seemed dark blue at first, and became pale violet after being left in the solution.

In pure water, the product was pink, but when dried, it gained a tinge of blue. If the solvent ratio was lower than 1:1, the color of the formed soap was pink as in pure water. When the ratio exceeded 1:1, although the formed soap was also pink at the beginning, often small blue particles grew overnight within pink precipitates. Sometimes the whole soap turned blue in a short time, less than an

3) A. E. Koenig, *J. Am. Chem. Soc.*, **36**, 951 (1914).
4) W. F. Whitmore and M. Lauro, *Ind. Eng. Chem.*, **22**, 646 (1930).

hour. These color changes were most rapid at a solvent ratio somewhat higher than 1 : 1.

**Effect of Stirring.**—As stated above, sometimes blue soap grew in addition to pink soap in the solution when it was left without stirring. First, we examined the effect of stirring on this color change.

In a standard procedure with the solvent ratio 5 : 1, pink soap turned blue without stirring, even if very slowly, but the color changed in 1 hr. with stirring. If some blue soap powder, prepared previously, was added to the solution, the color change was completed in 15 min.

When the solution was kept at 60°C after reaction, the color did not change even after 1 hr., but if it was taken out from the water-bath and cooled by stirring, the color began to change immediately and turned perfectly blue in 25 min.

From these facts, it is concluded that the blue soap has grown from pink soap. The addition of some blue soap advances the color change remarkably, for added soap powder forms nuclei for color change. At 60°C spontaneous occurrences of nuclei are suppressed, and the color change is not observed. Below 60°C nuclei of blue soap would appear, but they grow so slowly without stirring, that the color change proceeds locally and heterogeneously, and as a result small blue particles appear within pink precipitates. Therefore, to change color completely, cooling the solution by stirring is absolutely necessary.

The bubbling of air into the solution did not alter the speed of color change. Closing the vessel and stirring by a magnetic stirrer also did not influence the effect. It is evident that oxidation is not a cause of color change.

**Effect of Solvent Ratio.**—Next we examined again the effect of the solvent ratio on the color change, but with stirring.

Stearic acid (2 g.) was dissolved in ethanol and/or water (250 ml.) and neutralized by 0.15 N potassium hydroxide in ethanol or water (about 50 ml.). The solution was mixed at 60°C with cobalt chloride in ethanol and/or water (50 ml.), with various solvent ratios, and cooled by stirring. The time needed to turn blue was observed. The results are shown in Table I.

In series I, with larger solvent ratios, the colors of the products seemed violet or pale blue from an early stage. They did not readily turn blue and contained some white powder of potassium soap. Below the ratio 6 : 1, pink soap was formed at the beginning and changed blue soon, as stated before.

In series II, which contained more water than series I, the speed of the color change became larger with the lower solvent ratio. Sometimes blue soap turned violet soon and became red overnight. The red cobalt stearates formed in these systems are completely different in appearance from pink soaps formed directly after the reaction. When dried, they can be pulverized very easily, in contrast to plastic pink soaps.

TABLE I. EFFECT OF THE SOLVENT RATIO ON THE COLOR OF COBALT SOAPS

| System | No. | Solvent ratio based on volume | Color of product |
|---|---|---|---|
| | 1 | (pure ethanol) | Bluish precipit. in blue soln., mixed with white K soap. |
| | 2 | 30 : 1 | Pale violet, turned blue in 2.5 hr., mixed with K soap. |
| Series I | 3 | 15 : 1 | Violet, turned blue in 60 min., mixed with K soap. |
| | 4 | 9 : 1 | Reddish, turned blue in 60 min. |
| | 5 | 6 : 1 | Pink, turned blue in 60 min. |
| | 6 | 5 : 1 | Pink, turned blue in 30 min. |
| | 7 | 4 : 1 | Pink, turned blue in 15 min., violet in 60 min., red overnight. |
| Series II | 8 | 3.3 : 1 | Pink, turned blue in 15 min., violet in 40 min., red overnight. |
| | 9 | 2.8 : 1 | Pink, turned blue in 30 min. |
| | 10 | 2.3 : 1 | Pink, turned blue in 25 min. |
| | 11 | 2 : 1 | Pink, turned blue in 10 min., red overnight. |
| Series III | 12 | 1.5 : 1 | Pink, turned blue in 5 min., red overnight. |
| | 13 | 1.3 : 1 | Pink, turned blue in 10 min., red overnight. |
| | 14 | 1 : 1 | Pink, turned red overnight. |
| | 15 | 1 : 1.5 | Pink, turned red overnight. |
| Series IV | 16 | 1 : 2 | Pink, turned red overnight. |
| | 17 | 1 : 3 | Red, without change. |
| | 18 | 1 : 5 | Red, without change. |

In series III, with the greater water content, the speed of the color change became very rapid, and at the solvent ratio of about 1.5 : 1, it was at a maximum. The products turned completely red overnight.

The last series, where the solvent ratio is lower than 1 : 1, was very different from the preceding series. In this series soaps did not change blue, however long stirred, but became red gradually. The systems which contained the most little amount of ethanol were red rather than pink from the outset. It was hard to dry them in vacuum, for they contained a large amount of water.

Together with the other results obtained, the following facts were confirmed:

(i) The color of the product is determined by the solvent ratio after mixing. The addition of either solvent to the solution after reaction did not affect the color.

(ii) If the resultant solvent ratio is the same, the compositions of the reactant solutions are indifferent to the color of the product.

(iii) The extent of excess of cobalt chloride over stearic acid and the order of mixing solutions did not significantly affect the color of the soap formed.

(iv) The speed of the color change from blue to red depends on the solvent ratio and the time of stirring. Blue soap always turned red if it was left in solution for long a time.

**Effect of Degree of Neutralization.**—In these experiments, the solution of stearic acid was exactly neutralized by an alkaline solution. Next we examined the effect of the degree of neutralization on the color change of cobalt soap.

At the solvent ratio 1 : 2, when exactly neutralized, the cobalt soap did not change blue, though it later became red. If the amount of added alkaline solution was varied between 60 and 140% of the equivalent, different effects were observed. When the system was insufficiently neutralized, the products became red sooner and contained much free fatty acid. When the added alkali was more deficient, the color change became slower. However, when an excess of alkali was added to the system, the product became violet. When there is a large excess of alkali, the reaction would not readily proceed because, as will be discussed in the next part, the cobalt soap may be decomposed to free acid by the presence of much alkali.

At the solvent ratio 2 : 1, when exactly neutralized, the formed pink soap soon became blue with stirring and later turned red in the solution. But when alkali was added in excess, a color change from pink to blue was not observed and the soap turned red at last. On the contrary, when alkali was insufficient, the speed of becoming blue was more rapid. When the degree of neutralization was lower, the color change became quicker, although the yield was smaller.

As well as adding insufficient alkali to the fatty acid solution, the addition of hydrochloric acid to the cobalt chloride solution had the same effect on color change. But after the forming of the pink soap, the addition of hydrochloric acid was not effective.

From these results it is concluded that the solution must be acidic at mixing for realizing the color change.

**Effect of Using Other Solvents than Ethanol.**—Throughout the preceding experiments, the solvent was a mixture of ethanol and water. Next we used acetone and methanol in place of ethanol. Any solvent which dissolves fatty acid may be used, but when the solvent does not mix with water, as the petroleum ether used by Kaufmann and Lüssling[2], the procedure becomes somewhat difficult. With methanol or acetone, metathesis could be carried out as with ethanol. In particular, when the solvent ratio was lower than 1 : 1, only pink soaps were formed. With these solvents, even if the solvent ratio was higher than 1 : 1, the blue soap could not be obtained. But when acetone was used, the formed soap became red quickly.

**Effect of Using Other Cobalt Salts than Chloride.**—Instead of cobalt chloride we tried to use other cobalt salts. Cobalt nitrate and sulfate may be used in the same way as chloride. But cobalt acetate showed somewhat different effects.

Cobalt acetate may react directly with stearic acid in aqueous ethanol. In this substitution reaction, when the solvent ratio is 2 : 1, the color changed blue and subsequently turned red. But at the ratio 1 : 2, the color did not change at all.

The color change was suppressed markedly by the addition of alkali. If the fatty acid was exactly neutralized, that is, in metathesis, the formed pink soap did not change blue in any solvent ratio.

At the solvent ratio 2 : 1, pink soap made by metathesis turned blue in 60 min. with cobalt chloride, in 30 min. with cobalt nitrate, in 20 min. with cobalt sulfate, and never with cobalt acetate.

In a substitution reaction with cobalt acetate, the addition of alkali suppressed markedly the color change to blue. The substitution reaction could be carried out between cobalt acetate and stearic acid with acetone in place of ethanol.

However, when acetone was used, with the solvent ratio 2 : 1, pink soap turned blue, even if very slowly, but perfectly blue soap was not obtained.

**Effect of Using Other Fatty Acids than Stearic Acid.**—Other cobalt soaps may be prepared by metathesis in the same way as stearate. In place of stearic acid, palmitic, myristic, and lauric acid were used.

These reactions proceeded just the same way as with stearate. The color changes were also observed, but the speed of color change from pink to blue becomes slower, as the chain length of fatty acid decreases. The laurate could not turn blue under the same conditions.

The time for turning blue with the solvent ratio is tabulated in Table II. These reactions were obtained by stirring the solutions at 45°C for 1 hr. and later leaving them in the solution without stirring. The solutions were slightly acidic.

TABLE II. TIME FOR TURNING BLUE OF PINK COBALT SOAPS

| Solvent ratio | 4 : 1 | 1.5 : 1 | 1 : 1.5 | 1 : 4 |
|---|---|---|---|---|
| Cobalt stearate | 15 min. | 10 min. | — | — |
| Cobalt palmitate | 2 days | 1~2 hr. | — | — |
| Cobalt myristate | 4~5 days | 1 day | — | — |
| Cobalt laurate | — | — | — | — |

— Did not become blue.

**Summary**

As a method of preparation of cobalt soap, metathesis between alkaline soap and cobalt salt was investigated.

Cobalt stearate, palmitate and myristate were obtained in pink, blue and red forms according to conditions. Cobalt laurate in blue form was not observed.

Metathetic products were always pink at the beginning. If the system has a solvent ratio (solvent to water) higher than 1 : 1, and the solution after mixing is acidic, the color of soap will turn blue with stirring. It will change red later when left in the solution. The blue form could not be obtained with acetone or methanol as a solvent.

The speed of the color change became considerably slower with fatty acid of a shorter chain length.

In substitution reaction between stearic acid and cobalt acetate with a solvent ratio higher than 1 : 1, the same color changes were observed. But in this system the addition of some alkali suppressed markedly the color change, and at an exactly neutralized metathetic reaction the soap did not turn blue. Even in this case, when acetone was used instead of ethanol, the color change was observed, but the speed was very slow.

The author expresses his gratitude to Professor Bunnosuke Yamaguchi for his advice throughout this work and to Messrs. Itaru Mita, Hirokazu Watanabe and Hiroshi Kayano for their assistance in experiments.

*Institute for Science and Technology*
*The University of Tokyo*
*Meguro-ku, Tokyo*

---

# *Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. II. Compositions of Cobalt Soaps*

By Hirotaro KAMBE*

(Received February 27, 1961)

Cobalt soap is generally a neutral salt between a bivalent cobalt cation and two univalent fatty acid anions. For example, the composition of cobalt stearate is ideally expressed by $Co(C_{17}H_{35}COO)_2$.

Oudemans[1] and Caspari[2] have pointed out that cobalt laurate is monohydrate. Kaufmann and Lüssling[3] found that while, under some conditions, cobalt oleate was obtained as an acidic salt, $Co(C_{17}H_{33}COO)_2 \cdot (C_{17}H_{35}COO)_2$, cobalt stearate was a neutral salt.

In the previous part of these studies[4], it was found that cobalt soaps obtained by metathesis in aqueous ethanol showed three different colors, that is, pink, blue and red.

* Present address: Aeronautical Research Institute, the University of Tokyo, Meguro-ku, Tokyo.

1) A. C. Oudemans, *J. prakt. Chem.*, [1], **89**, 206 (1863).
2) C. E. Caspari, *Am. Chem. J.*, **27**, 310 (1902).
3) H. P. Kaufmann and Th. Lüssling, *Fette und Seifen*, **55**, 90 (1953).
4) H. Kambe, This Bulletin, **34**, 1786 (1961).

In the present part they will be analyzed. As a result, it will be ascertained that different colors are principally due to the difference of hydration of the cobalt soap.

## Experimental

**Materials.**—Cobalt soaps are cobalt stearates, described in the previous paper[4]. Several specimens of each typical color were chosen from among many samples.

**Analyses.**—*Free Fatty Acid.*—Free fatty acid was extracted from soaps by the use of acetone for 1 hr. with a Soxhlet extractor. The color of the soaps was not altered by extraction. Acetone was dehydrated by anhydrous potassium carbonate. A glass cylinder was inserted around a cylindrical filter paper in order to improve the circulation of the solvent[5]. The amount of free acid was determined by evaporating the solution. The residue was dissolved in ethanol, and the solution was titrated by a standard alkaline solution.

*Combined Fatty Acid.*—Cobalt soaps were decomposed by boiling with 0.1 N sulfuric acid. Isolated fatty acid and unreacted soap melted and floated in a mass on the surface of the solution. The decomposition was continued until the molten mass became wholly colorless.

Cobalt soap can be decomposed also by a 0.1 N alkaline solution. This method was not adequate here, however, because the solution foamed so much, that it was feared that unreacted soap might overflow the vessel.

The solution was cooled, and the seperated fatty acid was filtered off. The filtrate obtained in this process was used for determining the content of the cobalt. Fatty acid was dried on filter paper, dissolved in hot ethanol, and titrated by a standard alkaline solution.

*Cobalt.*—The amount of cobalt was determined by several methods. (i) Soaps were burnt to ashes, which were weighed as $Co_3O_4$. (ii) Cobalt was precipitated from the solution as a complex salt by $\alpha$-nitroso-$\beta$-naphthol. (iii) Cobalt was deposited on a platinum electrode electrolytically. (iv) The cobalt solution was titrated by an EDTA solution.

*Burning Method.*—Cobalt soap was heated in a porcelain crucible by a Bunsen burner. Stearic acid was carbonized at first, and then the whole mass was ignited and completely oxidized by strong heating. The residue was weighed as $Co_3O_4$.

*$\alpha$-Nitroso-$\beta$-naphthol Method.*—By adding an excess of hydrogen peroxide to the acidic solution of cobalt, cobalt ions were oxidized from bivalent to tervalent. The black cobaltic hydroxide precipitated from the solution by the addition of a sodium hydroxide solution. The precipitate was dissolved again by glacial acetic acid, and the dark brown solution obtained was diluted with some warm water and mixed with the solution of $\alpha$-nitroso-$\beta$-naphthol in acetic acid. The reddish brown precipitate was filtered off, dried at 130 C, and weighed as $(C_{10}H_6ONO)_3Co$.

*Electrodeposition Method.*—Cobalt stearate (0.1 g.) was decomposed by 0.1 N sulfuric acid (20 ml.), and the separated fatty acid was filtered off. The filtrate was concentrated to 10 ml., ammonium sulfate (0.5 g.) was added, and the solution was made alkaline with 0.1 N ammonia solution (40 ml.), and sodium bisulfate (0.02 g.) was added. With platinum plates as electrodes, the golden solution was electrolyzed with a current 0.2 amp. and 3.5 V. at 60°C for 8 hr. The cobalt metal deposited on the cathode was weighed after drying in an air-oven at 110°C.

*EDTA Titration.*—Cobalt soap (30 mg.) was decomposed by 0.3 N hydrochloric acid (20 ml.). The fatty acid was solidified to a mass. The solution was diluted to 70 ml. by water, murexide (ammonium purpurate) was added as an indicator[6], and the solution was neutralized by 1 N ammonia solution in some excess. The yellow solution was titrated by 0.01 M EDTA (disodium ethylenediamine tetraacetate), until the color of the solution became pink. The concentration of EDTA solution was calibrated by a standard cuprous nitrate solution.

*Water of Hydration.*—Cobalt soaps had been dried in a vacuum at room temperature. Pink species gained a tinge of blue, but other soaps did not change their colors substantially in this process. Their colors did not change during storage in an ambient atmosphere.

Inorganic cobalt salts contain some water of hydration, some of which could not be removed in the vacuum. It is possible for cobalt soaps to have such a tightly combined water of hydration. The water content was determined (i) by a Karl-Fischer reagent and (ii) by weighing after heating in a vacuum.

*Karl-Fischer Titration.*—From among the several methods of this technique, the inverse dead-stop method with "magic eye" titrometer was carried out[7]. The titration vessel was equipped with a draining cock, as proposed by Campbell[8].

The standard methanol used was an extra pure reagent, made by Takeda Chemicals Co., the water content of which was about 0.5% by volume. The Karl-Fischer reagent was prepared as usual[9] and calibrated by sodium acetate trihydrate.

The cobalt soaps did not dissolve, but were well dispersed in mixtures of methanol and pyridine, which were basic solvents of the reagent. However, because the soap was powder, it was difficult to place it in titration vessel. This was the main origin of errors.

*Dehydration in Vacuum at Heating.*—The decrease of weights was measured by a quartz spring balance in an evacuated glass tube at $10^{-3}$ mmHg. An electric furnace was used to heat the soap up to 150 C. The sensitivity of the quartz balance was 7.54 cm./g., and its accuracy was 0.2 mg. in weight. A sample of 0.1 g. was usually taken for measurements.

5) K. J. Mysels, H. H. Pomeroy and G. H. Smith, *Anal. Chem.*, **20**, 878 (1948).

6) H. Flaschka, *Mikrochemie*, **39**, 38 (1952).
7) R. Kieselbach, *Anal. Chem.*, **21**, 1578 (1949).
8) D. E. Campbell, ibid., **25**, 203 (1953).
9) J. Mitchell, Jr., and D. M. Smith, "Aquametry", Interscience Publishers, Inc., New York (1948).

## Results and Discussion

**Free Fatty Acid.**—The amounts of free fatty acid in several samples of each species of cobalt stearate were measured. The average values are shown in Table I. The amount of free acid was relatively little. It was most in pink, but very little in red, soap. The following analyses were carried out with samples, the free acid of which had been completely extracted.

Table I. Free fatty acid contents in cobalt stearates

| | |
|---|---|
| Pink | 4.14 % |
| Blue | 2.36 % |
| Red | 0.70 % |

**Compositions.**—Several analyses of each species of cobalt stearate were executed by various methods. These results are tabulated together in Table II. Although the values were scattered in some ranges, the average values of each method and their mean are shown.

Theoretical compositions calculated from several possible formulas of cobalt stearate are shown in Table III. In comparing Table II with Table III, it is certain that three forms of cobalt stearate are neither basic nor acidic salt.

The blue form corresponds to anhydrous neutral soap, for it shows no water content. The red form must be dihydrate, judging from the content of hydration water. The observed

Table II. Observed compositions of cobalt stearates

| | Cobalt, % | | | | Stearic acid, % | Hydration water, % | | Total, % |
|---|---|---|---|---|---|---|---|---|
| | By burning to ashes | With α-nitroso-β-naphthol | By electro-deposition | By EDTA titration | By neutral-ization | By Karl-Fischer reagent | By heating in vacuum | |
| | 8.12 | 9.1 | 9.29 | | 82.6 | | 3.56 | |
| | 8.95 | 9.4 | 9.65 | | 87.0 | | 4.55 | |
| | 9.01 | 9.4 | 9.12 | | 81.8 | | 3.97 | |
| | | 10.8 | 9.52 | | 85.5 | | 6.34 | |
| Pink | | 12.1 | 9.25 | | 87.3 | | 3.91 | |
| | | 9.0 | | | | | 3.71 | |
| | | | | | | | 4.35 | |
| | | | | | | | 6.26 | |
| | | | | | | | 3.65 | |
| | av. 8.65 | av. 10.0 | av. 9.38 | | av. 84.8 | | av. 4.36 | |
| | | mean 9.34 | | | mean 84.8 | | mean 4.36 | mean 98.50 |
| | 8.94 | | 9.35 | 9.32 | 88.0 | −0.8 | 0.0 | |
| | 10.43 | | 10.15 | 9.63 | 90.9 | −0.5 | | |
| | 9.91 | | 10.15 | 9.59 | 92.5 | 1.4 | | |
| Blue | | | 10.33 | 9.34 | 91.5 | 0.26 | | |
| | | | 10.78 | 9.51 | 88.1 | | | |
| | | | 9.78 | 9.58 | 89.1 | | | |
| | | | 10.12 | 9.48 | 92.4 | | | |
| | | | 10.54 | | | | | |
| | av. 9.76 | | av. 10.14 | av. 9.49 | av. 90.4 | av. 0.1 | | |
| | | mean 9.80 | | | mean 90.4 | mean 0.0 | | mean 100.20 |
| | 7.88 | | 9.04 | 9.04 | 84.5 | 3.46 | 5.43 | |
| | 9.65 | | 9.11 | 9.21 | 86.0 | 4.40 | 5.67 | |
| | 8.24 | | 9.36 | 9.11 | 86.9 | 1.28 | 5.41 | |
| | 8.57 | | 9.18 | 9.01 | 78.6 | 5.48 | 5.72 | |
| Red | | | 9.26 | 9.01 | 87.6 | | | |
| | | | 9.71 | 9.02 | 87.6 | | | |
| | | | | 9.04 | | | | |
| | | | | 9.06 | | | | |
| | av. 8.65 | | av. 9.34 | av. 9.06 | av. 85.1 | av. 3.66 | av. 5.56 | |
| | | mean 9.02 | | | mean 85.1 | mean 4.61 | | mean 98.73 |

TABLE III. CALCULATED COMPOSITIONS OF COBALT STEARATES

| | Cobalt, % | Stearic acid, % | Water, % |
|---|---|---|---|
| Neutral salts, $(C_{17}H_{35}COO)_2Co$ | 9.42 | 90.58 | — |
| Monohydrate, $(C_{17}H_{35}COO)_2Co \cdot H_2O$ | 9.15 | 88.05 | 2.80 |
| Dihydrate, $(C_{17}H_{35}COO)_2Co \cdot 2H_2O$ | 8.90 | 85.64 | 5.46 |
| Basic salt, $(C_{17}H_{35}COO)Co(OH)$ | 16.40 | 83.60 | — |
| Acidic salt, $(C_{17}H_{35}COO)_2Co(C_{17}H_{35}COOH)$ | 6.47 | 93.53 | — |

contents of cobalt of these soaps were somewhat larger than the calculated values, for some of the combined fatty acid might be hydrolyzed and removed during the extraction by acetone.

The pink form shows a composition nearer to red dihydrate than to blue anhydrate. Experimental values are particularly scattered in this species. As the pink soap is an incipient product in metathesis, it may be natural that its composition is somewhat indefinite.

**Mechanism of Color Change.**—From these results, it has been ascertained that the difference of color is due to the degree of hydration of these soaps. In the previous paper[4], it was found that under some conditions the pink soap thus formed soon turned blue and then red later in solution. This corresponds with the change of the amount of water of hydration, which first decreases and then increases again. This process seems very strange, but the following interpretation may be proposed.

The alkaline soap in aqueous ethanol takes the form of micelles, in which lyophilic ionic groups of soap molecules exist in the outer layer against solvent molecules. Ionic groups dissociate in different degrees, according to the solvent ratio in solution. When the cobalt ions are added, dissociated soap ions in the outer lyophilic layer react with cobalt ions immediately. Therefore, in the incipiently formed pink soap there remains the original micelle structure of alkaline soap, as will be discussed in the later part of these studies.

With the existence of sufficient alkali, cobalt soap turns gradually to red dihydrate, which is the most stable form in these solvents. When the alkali is insufficient, the dissociation of alkaline soap is greatly suppressed, and therefore the ionic reactions proceed limitedly. In these circumstances the yield of cobalt soap is little, and much free acid exists in the formed soap.

When the solvent ratio is higher than 1 : 1, the solvent becomes somewhat oleophilic and the formed pink soap turns blue, perhaps by an inversion of the micelle structure. In this case some of the lyophobic hydrocarbon chains appear outside. As the soap becomes less lyophilic in this system, blue crystals tend to rise to the surface of the solution.

In the following time, water molecules gradually penetrate into the interior of the micelles of blue soap and adhere to the hydrophilic cobalt ions as waters of hydration. As the penetration of water is difficult through such a thick layer of hydrocarbon chains, the change of color from blue to red generally occurs slowly.

## Summary

Pink, blue and red cobalt stearates were analyzed and their compositions were determined. From these results, it has been confirmed that blue soap is anhydrate and red soap is dihydrate. The pink soap has a rather indefinite composition nearer to red soap. A mechanism of the color changes was proposed based on the inversion of the micelle structure under some circumstances.

The author expresses his gratitude to Professor Bunnosuke Yamaguchi for his kind advice throughout this work. He is also indebted to Mr. Itaru Mita for his executions of EDTA titrations, and to Messrs. Hirokazu Watanabe, Satoshi Ayano and Takeo Ozawa for their assistance on experiments.

*Institute for Science and Technology*
*The University of Tokyo*
*Meguro-ku, Tokyo*

# *Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. III. Spectrophotometric Specifications of Colors of Cobalt Soaps*

By Hirotaro KAMBE

(Received February 28, 1961)

Cobalt soaps of higher saturated fatty acids have been described generally as pink crystals. Recently Herron and Pink[1] described rose-pink cobalt laurate dihydrate and purple anhydrate, which was obtained by the dehydration of pink soap in boiling organic solvents.

In a previous paper of this series[2], three species of cobalt soap of different colors were obtained by metathesis in aqueous ethanol under some conditions. From results of analyses, it was ascertained that blue soap is anhydrate, red soap is dihydrate, and pink soap has a degree of hydration near to that of dihydrate[3].

In the present paper, the colors of these soaps will be specified by spectrophotometry. Reflection spectra and a chromaticity diagram of these colors will be shown. Relations of these colors with each other will also be discussed.

## Experimental

**Materials.**—The same samples of cobalt stearates were used as for the previous papers[2,3].

**Reflection Spectra.**—Reflection spectra of soaps were measured with a Shimadzu QR-50 quartz spectrophotometer, to which an integrating sphere was attached. Reflection coefficients expressed in percentages were plotted against wavelengths between 350 and 700 mμ to get reflection curves.

**Graphical Representation of Chromaticity.**—Reflection curves were analyzed by a method proposed by the International Commission on Illumination (I.C.I.)[4]. Tristimulus values, $X$, $Y$ and $Z$, were determined from reflection curves by graphical integrations with the thirty-selected-ordinate method[4].

$$X=0.03268\sum R_x(\lambda_n) \qquad Y=0.03333\sum R_y(\lambda_n)$$
$$Z=0.03938\sum R_z(\lambda_n) \qquad (1)$$

where $R(\lambda_n)$'s are reflection coefficients of the sample at selected wavelengths (Table I).

Trichromatic coefficients, $x$, $y$ and $z$ were calculated by the formulas

$$x=\frac{X}{X+Y+Z} \qquad y=\frac{Y}{X+Y+Z}$$

Table I. Thirty selected ordinates for illuminant C

| Ordinate number | $(X)$ Wavelength mμ | $(Y)$ Wavelength mμ | $(Z)$ Wavelength mμ |
|---|---|---|---|
| 1 | 424.4 | 465.9 | 414.1 |
| 2 | 435.5 | 489.4 | 422.2 |
| 3 | 443.9 | 500.4 | 426.3 |
| 4 | 452.1 | 508.7 | 429.4 |
| 5 | 461.2 | 515.1 | 432.0 |
| 6 | 474.0 | 520.6 | 434.3 |
| 7 | 531.0 | 525.4 | 436.5 |
| 8 | 544.3 | 529.8 | 438.6 |
| 9 | 552.4 | 533.9 | 440.6 |
| 10 | 558.7 | 537.7 | 442.5 |
| 11 | 564.1 | 541.4 | 444.4 |
| 12 | 568.9 | 544.9 | 446.3 |
| 13 | 573.2 | 548.4 | 448.2 |
| 14 | 577.3 | 551.8 | 450.1 |
| 15 | 581.3 | 555.1 | 452.1 |
| 16 | 585.0 | 558.5 | 454.0 |
| 17 | 588.7 | 561.9 | 455.9 |
| 18 | 592.4 | 565.3 | 457.9 |
| 19 | 596.0 | 568.9 | 459.9 |
| 20 | 599.6 | 572.5 | 462.0 |
| 21 | 603.3 | 576.4 | 464.1 |
| 22 | 607.0 | 580.5 | 466.3 |
| 23 | 610.9 | 584.8 | 468.7 |
| 24 | 615.0 | 589.6 | 471.4 |
| 25 | 619.4 | 594.8 | 474.3 |
| 26 | 624.2 | 600.8 | 477.7 |
| 27 | 629.8 | 607.7 | 481.8 |
| 28 | 636.6 | 616.1 | 487.2 |
| 29 | 645.9 | 627.3 | 495.2 |
| 30 | 663.0 | 647.4 | 511.2 |

$$z=\frac{Z}{X+Y+Z} \qquad (2)$$

They were plotted on an I.C.I. chromaticity diagram. Dominant wavelength $\lambda_d$, purity $p_c$, and brightness $Y$ were determined for each sample.

## Results and Discussion

The reflection spectra of several samples of each typical color are shown in Figs. 1—3. Their tristimulus values and trichromatic coefficients have been calculated in Table II and plotted on an I.C.I. chromaticity diagram in Fig. 4. Their dominant wavelengths, purities,

* Present address: Aeronautical Research Institute, The University of Tokyo, Meguro-ku, Tokyo.

1) R. C. Herron and R. C. Pink, *J. Chem. Soc.*, **1956**, 3948.
2) H. Kambe, This Bulletin, **34**, 1786 (1961).
3) H. Kambe, ibid., **34**, 1790 (1961).
4) A. C. Hardy, "Handbook of Colorimetry", Cambridge, Mass. (1936).

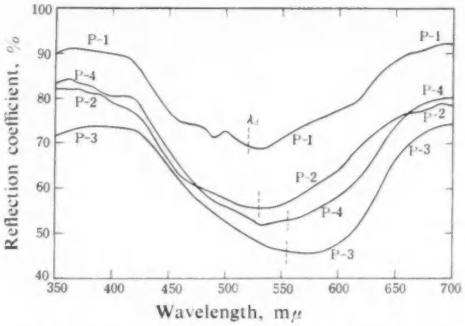



Fig. 1. Reflection curves of pink cobalt stearates.

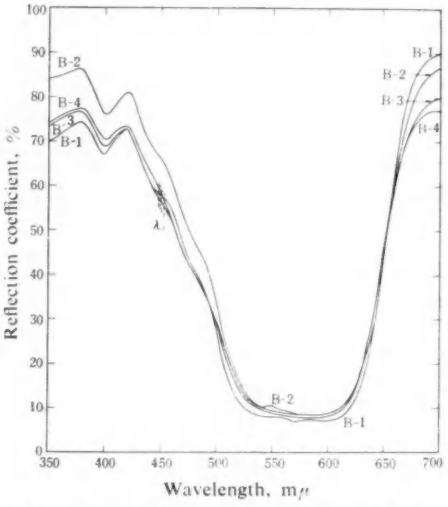



Fig. 2. Reflection curves of blue anhydrous cobalt stearates.

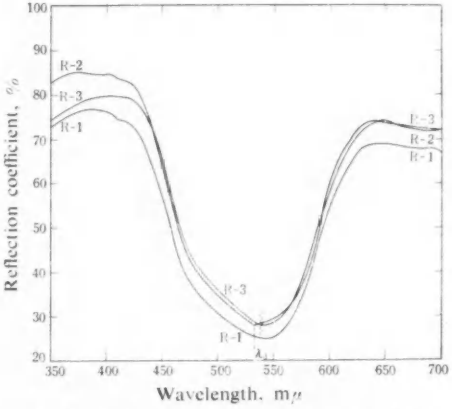



Fig. 3. Reflection curves of red cobalt stearate dihydrates.

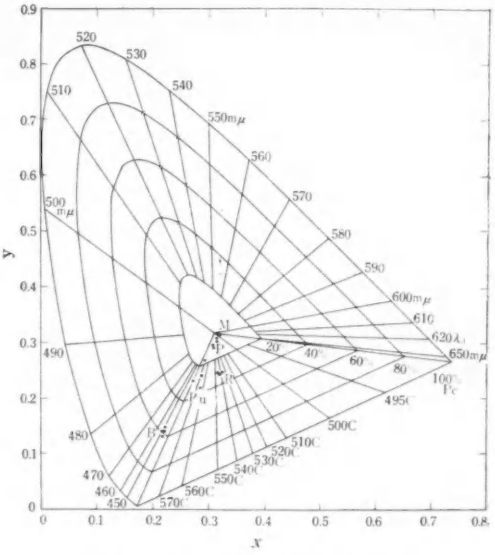



Fig. 4. I.C.I. chromaticity diagram.

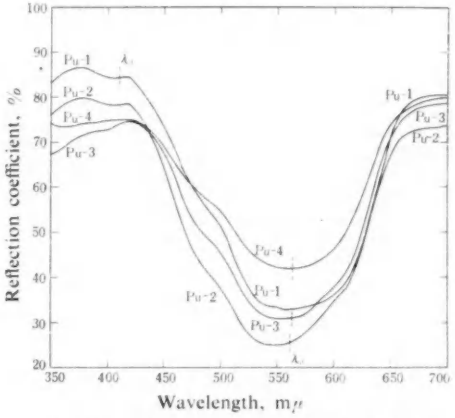



Fig. 5. Reflection curve of purple cobalt stearates.

and brightnesses are also tabulated in Table II.

The dominant wavelengths $\lambda_d$ of each spectrum are shown with dotted lines. In color language, blue and red soaps must be called violet and magenta respectively.

Pink soaps (Fig. 1) show a broad absorption band with a maximum at 530~540 mμ. The dominant wavelength of pink soaps varies within a wide range, from pure pink at 520c mμ to bluish pink at 565c mμ, but it does not essentially differ from that of red soaps. Pink soaps have smaller purities and larger brightnesses than red soaps.

TABLE II. CHROMATICITY COEFFICIENTS OF COLORS OF SEVERAL TYPICAL COBALT STEARATES

| System | Tristimulus values | | | Trichromatic coefficients | | | Dominant wavelength | Purity | Brightness |
|---|---|---|---|---|---|---|---|---|---|
| | $X$ | $Y$ | $Z$ | $x$ | $y$ | $z$ | $\lambda_d$, m$\mu$ | $p_c$, % | $Y$, % |
| (Pink soaps) | | | | | | | | | |
| P-1 | 76.24 | 73.81 | 91.78 | 0.315 | 0.305 | 0.380 | 520c* | 5.5 | 73.81 |
| P-2 | 63.38 | 59.74 | 77.52 | 0.316 | 0.298 | 0.386 | 530c | 8.5 | 59.74 |
| P-3 | 67.13 | 63.79 | 86.23 | 0.309 | 0.294 | 0.397 | 554c | 9.0 | 63.79 |
| P-4 | 59.65 | 55.86 | 77.89 | 0.308 | 0.289 | 0.403 | 555c | 10.5 | 55.86 |
| (Blue soaps) | | | | | | | | | |
| B-1 | 21.26 | 12.67 | 64.43 | 0.216 | 0.129 | 0.655 | 448 | 62.5 | 12.67 |
| B-2 | 24.45 | 15.45 | 73.07 | 0.216 | 0.137 | 0.647 | 452 | 60.5 | 15.45 |
| B-3 | 21.76 | 13.74 | 63.20 | 0.220 | 0.139 | 0.641 | 449 | 57.0 | 13.74 |
| B-4 | 22.63 | 14.78 | 64.49 | 0.222 | 0.145 | 0.633 | 450 | 56.5 | 14.78 |
| (Red soaps) | | | | | | | | | |
| R-1 | 48.84 | 36.22 | 62.96 | 0.330 | 0.245 | 0.425 | 533c | 32.5 | 36.22 |
| R-2 | 53.78 | 40.25 | 71.30 | 0.325 | 0.243 | 0.431 | 538c | 32.5 | 40.25 |
| R-3 | 53.34 | 40.25 | 71.21 | 0.324 | 0.244 | 0.432 | 540c | 31.5 | 40.25 |

* 520c m$\mu$ means complementary to color of 520 m$\mu$.

TABLE III. CHROMATICITY COEFFICIENTS OF SOME PURPLE COBALT STEARATES AND PINK COBALT STEARATES OBTAINED IN AQUEOUS METHANOL

| System | Tristimulus values | | | Trichromatic coefficients | | | Dominant wavelength | Purity | Brightness |
|---|---|---|---|---|---|---|---|---|---|
| | $X$ | $Y$ | $Z$ | $x$ | $y$ | $z$ | $\lambda_d$, m$\mu$ | $p_c$, % | $Y$, % |
| (Purple soaps obtained from blue soaps) | | | | | | | | | |
| Pu-1 | 46.22 | 39.17 | 84.23 | 0.272 | 0.231 | 0.497 | 410 | 27.5 | 39.17 |
| Pu-2 | 39.06 | 29.53 | 67.90 | 0.286 | 0.216 | 0.497 | 561c | 36.0 | 29.53 |
| (Purple soaps obtained from red and pink soaps) | | | | | | | | | |
| Pu-3 | 45.26 | 37.66 | 74.94 | 0.287 | 0.239 | 0.475 | 562c | 27.0 | 37.66 |
| Pu-4 | 52.34 | 47.41 | 78.73 | 0.293 | 0.266 | 0.441 | 564c | 17.0 | 47.41 |
| (Pink soaps obtained in aqueous methanol) | | | | | | | | | |
| M-1 | 83.21 | 81.61 | 95.46 | 0.320 | 0.314 | 0.367 | 493c | 3.0 | 81.61 |
| M-2 | 85.91 | 84.42 | 98.34 | 0.320 | 0.314 | 0.366 | 493c | 3.0 | 84.42 |

Blue anhydrates (Fig. 2) show a large absorption band with a broad maximum at 580~590 m$\mu$, and a shallow but sharp absorption band at 400 m$\mu$. The blue color of this species originates from a large reflection at shorter wavelengths.

Red dihydrates (Fig. 3) show a deep but relatively sharp absorption band at 540~550 m$\mu$. Sometimes the spectra of blue soaps have a small shoulder at a corresponding position, arising from the red soap also present.

When blue soap was taken out of the solution at a half-turned-red state, purple soap was obtained. Pink and red soaps also became purple when they were immersed in pure ethanol for a long time. These samples are shown in Figs. 4 and 5, and their trichromatic coefficients are tabulated in Table III.

Purple soaps have dominant wavelengths between those of pink and blue soaps. Purple soaps obtained from blue soap have relatively larger purities. In these samples the dominant wavelength seems to change abruptly from 564c m$\mu$ to 410 m$\mu$, but it is clear from the chromaticity diagram (Fig. 4) that these dominant wavelengths are continuous. The main origin of purple color changes in this range, however, from an absorption band at 560 m$\mu$ to a reflection band at 400 m$\mu$.

In this way, it is established that among cobalt soaps of different colors, red and pink soaps are the same in nature, although their colors differ in purity and brightness, and that blue soap continues to pink or red soap through purple soaps.

Cobalt stearate may be formed by metathesis in aqueous methanol instead of ethanol[2], but the color of the soaps thus formed is pale pink. Their reflection curves are very flat, with a maximum at about 500 m$\mu$, as shown in Fig. 6 and in Table III. It is characteristic for them that their purities are small and

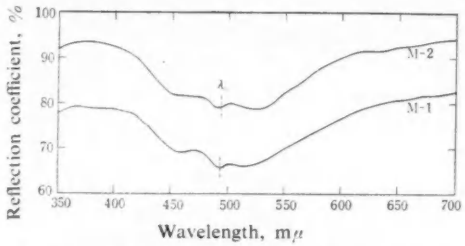



Fig. 6. Reflection curves of cobalt stearates obtained in aqueous methanol.

their brightnesses are large, and their maximum absorption occurs at a shorter wavelength.

**Summary**

The colors of three species of cobalt stearates were specified by I. C. I. chromaticity coefficients. Reflection spectra have been compared with each other, and it has been found that these colors are continuous in nature.

Pink soaps have dominant wavelengths in a wide range from 520c~555c mμ and show small purities and large brightnesses. Red soaps have essentially the same dominant wavelengths as that of pink soaps at 530c~540c mμ, but they show comparatively large purities and small brightnesses, because they are darker than pink soaps. They must be called magenta in color language.

Blue soaps must be called violet rigorously, for they show dominant wavelengths at about 450 mμ. They have larger purities and smaller brightnesses. Between blue and pink, many tones of color from violet to purple exist continuously. It is certain that these colors are related to each other.

The pale pink cobalt stearates obtained in aqueous methanol were specified in the same way.

The author expresses his gratitude to Professor Bunnosuke Yamaguchi, for his advice throughout this work. He is also indebted to Messrs. Hiroshi Kayano and Teijiro Mizuno for their assistance in spectrophotometry.

*Institute for Science and Technology*
*The University of Tokyo*
*Meguro-ku, Tokyo*

---

# *Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. IV. Ionic Nature of Cobalt Soaps, Revealed in Infrared Absorption Spectra and Magnetic Susceptibilities*

By Hirotaro KAMBE* and Itaru MITA*

(Received March 11, 1961)

In the previous papers of these studies[1-3], three forms of cobalt soap with different colors —in other words, with different degrees of hydration—were found. As they are salts of fatty acid, they must be composed of cobalt and fatty acid ions.

In the present paper, their infrared absorption spectra and magnetic susceptibilities are measured. It is concluded that as the infrared absorption bands of carboxylate ion are found, these soaps are essentially ionic in nature. Magnetic moments of cobalt ion in these soaps, calculated from magnetic susceptibilities, support this conclusion.

Infrared spectra of cobalt salts of normal fatty acids, from formic to stearic acid, were observed by Duval, Lecomte, and Douvillé[4]. They confirmed that the carboxylic groups in these salts are essentially ionic in nature.

Herron and Pink[5] measured the magnetic susceptibilities of cobalt stearate and laurate, and of cobalt laurate dihydrate. The magnetic moments of cobalt ions in these soaps were given as $\mu_{eff}=5.00$, 5.06 and 5.07 BM respectively. Moreau and Vatteroni[6] measured the magnetic susceptibilities of the cobalt salts of fatty acids with carbon numbers between 1

* Present address: Aeronautical Research Institute, The University of Tokyo, Meguro-ku, Tokyo.

1) H. Kambe, This Bulletin, **34**, 1786 (1961).
2) H. Kambe, ibid., **34**, 1790 (1961).
3) H. Kambe, ibid., **34**, 1794 (1961).
4) C. Duval, J. Lecompte and F. Douvillé, *Ann. phys.*, [11], **17**, 5 (1942).
5) R. C. Herron and R. C. Pink, *J. Chem. Soc.*, 1956, 3948.
6) C. Moreau and M. Vatteroni, *Compt. rend.*, **237**, 1090 (1953).

and 18. They have found that the susceptibilities of cobalt salts of higher fatty acids are somewhat larger than that of inorganic cobalt sulfate.

The experimental results obtained in the present paper will be discussed in comparison with these investigations.

## Experimental

**Materials.**—Cobalt stearate, palmitate, and myristate, of each typical color, obtained in the previous paper[1], were used as samples. Stearic acid, sodium stearate, and cobalt hydroxide, which had been purified as usual, were used references to the infrared investigations.

**Infrared Absorption Spectra.**—Infrared absorption spectra were measured chiefly with a Perkin Elmer Model 112 single beam spectrophotometer, using a sodium chloride or calcium fluoride prism. Some samples were measured also with a Perkin Elmer Model 12B double beam spectrophotometer at the Laboratories of Mitsubishi Kasei Co*2.

As cobalt soaps are generally insoluble in common solvents, powdered samples were used in the form of potassium bromide disks, or mulls in Nujol or in hexachlorobutadiene (HCB).

The potassium bromide disk method was used mainly in the range of wave number below 1700 $cm^{-1}$. The sample soaps and potassium bromide were carefully dried and pulverized to pass through a sieve of 200~250 meshes per inch. A small percentage was mixed with potassium bromide powder and pressed at 10,000 kg./$cm^2$ to form a disk.

Above 2700 $cm^{-1}$, the Nujol mull or HCB mull method was used exclusively. Mulls were placed between rock salt plates. Nujol shows strong absorptions of C-H bond, which overlap C-H absorptions of the soap. Although HCB is so volatile that it is difficult to make mulls with it, it was chiefly used in the range of 2700~4000 $cm^{-1}$, for it shows no absorption above 1700 $cm^{-1}$.

**Magnetic Constants.**—The magnetic susceptibility $\chi_H$ of cobalt soap, mixed with zinc oxide, was measured by Gouy's method*3. $\chi_H$ was corrected for ferromagnetic imprities by plotting susceptibilities against reciprocal field strength. Extrapolation to infinite field strength gives $\chi_\infty$, which is substantially free from ferromagnetic effects.

As the specific susceptibility of zinc oxide, $\chi_{ZnO}$, had been given as $-0.26\times10^{-6}$ c. g. s., the specific susceptibility of soap, $\chi$, was determined by the following formula:

$$\chi_\infty = \frac{w}{100}\chi + \frac{100-w}{100}\chi_{ZnO} \qquad (1)$$

in which $w$ is the concentration of soap in per cent by weight. Molar susceptibility is calculated by a formula:

$$\chi_M = M\cdot\chi \qquad (2)$$

in which $M$ is the molecular weight of soap.

*2 With the latter instrument, measurements were executed by Mr. S. Morita.

*3 Magnetic measurements were carried out by Dr. Y. Matsunaga at Department of Chemistry, Faculty of Science, The University of Tokyo.

The diamagnetic component of susceptibility, $\sum\chi_{dia}$, was corrected by a formula

$$\chi_M = \chi_{para} - \sum\chi_{dia} \qquad (3)$$

The diamagnetic susceptibilities of the constituents of which are shown in Table I.

The magnetic moments in Bohr magneton (BM) were calculated by a formula:

$$\mu_{eff} = 2.839\sqrt{\chi_{para}\cdot T} \quad (BM) \qquad (4)$$

TABLE I. SPECIFIC DIAMAGNETIC SUSCEPTIBILITIES, $-\chi_{dia}\cdot10^6$ (c.g.s./g.)

| | |
|---|---|
| Stearate ion | 209* |
| Hydration water | 13[7] |
| Cobalt(II) ion | 12[8] |

* This value was found in magnesium, zinc and cadmium stearates[7].

## Results and Discussion

**Infrared Absorption Spectra.**—The wave numbers of the absorption maxima in the infrared spectra of cobalt soaps are assigned and tabulated in Tables II and III.

*Absorptions by Hydrocarbon Chain.*—Among species of the same color, the chain length of fatty acid did not significantly influence the spectrum. Band progression at 1200~1300 $cm^{-1}$, due to hydrocarbon chain, depends to some extent upon the length of the chain, but the absorption bands of cobalt soaps are weaker than that of stearic acid.

The absorption bands of C-H stretching vibrations, i. e. the out-of-phase vibration of $CH_2$ at 2865, the in-phase one at 2935, and the asymmetrical vibration of $CH_3$ at 2970 $cm^{-1}$, and the bands of symmetrical bending of $CH_2$ at 1465 $cm^{-1}$ were always observed in all soaps, without distinction of color. The symmetrical bending vibration band of $CH_3$ at 1375 $cm^{-1}$ was found in red soaps, but in other soaps it was not readily indentified.

*Absorptions by Carboxylate Ion.*—Absorption spectra in the range of 1250~1800 $cm^{-1}$ are shown in Figs. 1—3.

It is well known that in free fatty acid carboxyl groups of two molecules are donded by hydrogen bonds to take a dimeric form. The absorption of a carboxyl group in this state reveals its C=O stretching vibration band near 1700 $cm^{-1}$ (cf. Table III). In cobalt soaps, two absorption bands of carboxyl group were found at 1400 and 1550 $cm^{-1}$, instead of one band at 1700 $cm^{-1}$. They correspond to the symmetric and antisymmetric stretching vibrations of carboxylate ion, $-\left[C\begin{smallmatrix}O\\O\end{smallmatrix}\right]^-$, as

7) M. Prasad, C. R. Kanekar, S. P. Walvekar and D. D. Khanolkar, *J. Chem. Phys.*, **18**, 936 (1950).
8) P. W. Selwood, *Chem. Revs.*, **38**, 41 (1946).

TABLE II. INFRARED ABSORPTION SPECTRA OF COBALT SOAPS MEASURED WITH A P. E. 112 SPECTROPHOTOMETER ($cm^{-1}$)*

| System | Progression bands | | | | | Sym. bend. $CH_3$ | Sym. str. $COO^-$ | Asym. bend. $CH_3$ | Sym. bend. $CH_2$ | Asym. str. $COO^-$ | Out-of-phase str. $CH_2$ | In-phase str. $CH_2$ | Asym. str. $CH_3$ | Str. OH | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Pink soaps) | | | | | | | | | | | | | | | |
| Cobalt stearate | w 1270 | w 1284 | w 1303 | w 1320 | w 1336 | | s 1410 | s 1441 | s 1467 | s 1559 | s 2870 | s 2940 | m 2970 | s 3300 | |
| Cobalt palmitate | w 1260 | w 1288 | w 1297 | w 1318 | w 1334 | | s 1410 | s 1441 | s 1467 | s 1559 | s 2870 | s 2940 | m 2970 | s 3290 | |
| Cobalt myristate | | w 1290 | | w 1316 | w 1334 | | s 1410 | s 1441 | s 1467 | s 1559 | s 2870 | s 2940 | m 2970 | s 3300 | |
| (Blue soaps) | | | | | | | | | | | | | | | |
| Cobalt stearate | | w 1287 | 1307 | w 1322 | w 1340 | m 1396 | | | m 1461 | s 1525 | s 2860 | s 2935 | m 2970 | | |
| Cobalt palmitate | | | w 1297 | w 1322 | w 1340 | m 1396 | | | m 1461 | s 1523 | s 2860 | s 2935 | m 2970 | | |
| Cobalt myristate | | | w 1296 | w 1322 | w 1341 | m 1396 | | | m 1461 | s 1523 | s 2860 | s 2935 | m 2970 | | |
| (Red soaps) | | | | | | | | | | | | | | | |
| Cobalt stearate | | w 1285 | w 1305 | w 1322 | w 1336 | w 1374 | s 1412 | | s 1470 | s 1535 | s 2865 | s 2935 | m 2970 | s 3260 | s 3400 |
| Cobalt palmitate | | w 1278 | w 1296 | w 1322 | w 1340 | w 1376 | m 1412 | | s 1469 | s 1534 | s 2865 | s 2935 | m 2970 | s 3260 | s 3400 |
| Cobalt myristate | | | w 1292 | w 1318 | w 1340 | m 1374 | s 1412 | | s 1468 | s 1532 | s 2865 | s 2935 | m 2970 | s 3260 | s 3400 |

TABLE III. INFRARED ABSORPTION SPECTRA OF COBALT SOAPS MEASURED WITH A P. E. 21B, BY KBr DISK METHOD ($cm^{-1}$)*

| System | Rocking $CH_2$ | | Out-of-plane deform. OH | Str. C-C | Progression bands | Sym. str. $COO^-$ | | Asym. bend. $CH_3$ | Sym. bend. $CH_2$ | Asym. str. $COO^-$ | Str. C=O | Str. OH | Out-of-phase str. $CH_2$ | In-phase str. $CH_2$ | Asym. str. $CH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Blue cobalt stearate | w 720 | | | w 1110 | v. w several | m 1400 | | | m 1468 | m 1532 | | | s 2850 | s 2920 | sh 2970 |
| Red cobalt stearate | w 720 | | | w 1110 | v. w several | m 1415 | | | m 1470 | s 1532 | | | s 2850 | s 2920 | sh 2970 |
| Sodium stearate | w 720 | | | v. w 1110 | v. w several | m 1424 | | m 1445 | m 1475 | s 1560 | | | s 2850 | s 2920 | sh 2960 |
| Stearic acid | m 720 | m 730 | m 940 | w 1110 | w 1190~1300 | m 1412 | m 1432 | | m 1468 | | s 1700 | d. m 2650 | s 2850 | s 2920 | sh 2960 |

* s: strong; m: medium; w: weak; v. w: very weak; sh: shoulder; d: diffuse

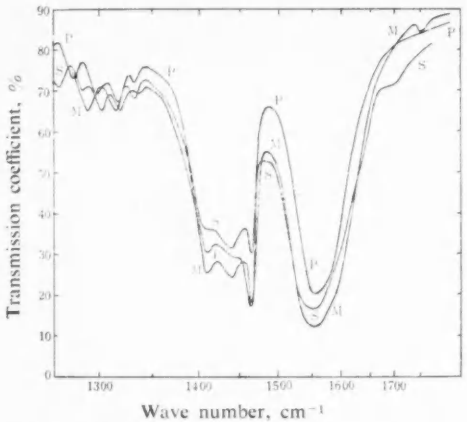



Fig. 1. Infrared absorption spectra of pink cobalt soaps.
S: Cobalt stearate P: Cobalt palmitate
M: Cobalt myristate

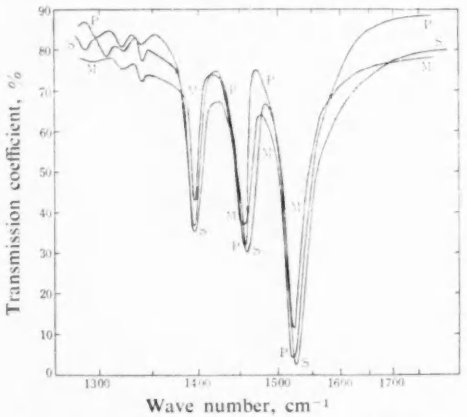



Fig. 2. Infrared absorption spectra of blue cobalt soaps.
S: Cobalt stearate P: Cobalt palmitate
M: Cobalt myristate

pointed out by Duval, Lecompte and Douvillé[4]. Their conclusion was based on the deformation vibration modes of carboxylate ions, appearing at lower frequency range than ours. Their results were stated to be uncertain at a higher frequency range owing to the insufficient resolving power of their instrument.

From this result it has been concluded definitely that all cobalt soaps obtained in our experiments are ionic in nature. As a reference, spectra of free stearic acid and sodium stearate are shown in Table III. Stearic acid distinctly shows a stretching vibration of C=O at 1700

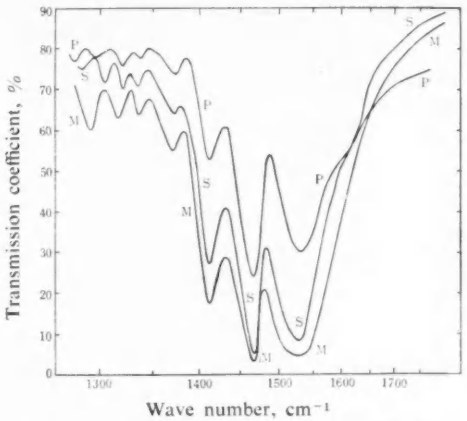



Fig. 3. Infrared absorption spectra of red cobalt soaps.
S: Cobalt stearate P: Cobalt palmitate
M: Cobalt myristate

$cm^{-1}$, while no band was found at 1550 $cm^{-1}$ corresponding to the antisymmetric vibration of carboxylate ion. In place of the symmetric stretching band of carboxylate ion at 1400 $cm^{-1}$, there appeared the C–O stretching band and O–H in-plane deformation band of $-C\begin{matrix}O\\OH\end{matrix}$. Naturally, the OH stretching band at 2650 $cm^{-1}$ and the OH out-of-plane deformation band at 940 $cm^{-1}$ appeared in the spectrum of stearic acid.

Sodium stearate shows carboxylate bands at 1424 and 1560 $cm^{-1}$ and an absorption by the asymmetrical bending of $CH_2$ at 1445 $cm^{-1}$, which appears in pink soaps, exclusively. This may indicate the similarity between sodium soap and pink cobalt stearate.

*Absorptions by Hydroxyl Bond.* — In spectra of cobalt soaps with different colors of the same fatty acid, several differences were found.

In red and pink soaps, absorptions by stretching vibration of OH bonds appeared in the 3200~3400 $cm^{-1}$ region, but in blue soaps they were completely lacking. This is in accordance with the results of analyses of water content[2]. In pink soaps, a broad peak reveals itself at 3300 $cm^{-1}$, but in red soap, two peaks appear at 3260 and 3400 $cm^{-1}$.

The hydroxyl bond of cobalt hydroxide shows a very sharp band of free OH vibration at 3640 $cm^{-1}$, which does not exist in the spectrum of every soap. Liquid water shows a peak of hydrogen-bonded OH at 3410 $cm^{-1}$. In comparison with these data, water molecules in cobalt soaps were attached to cobalt ion with stronger bonds than hydrogen-bonds in

TABLE IV. MAGNETIC CONSTANTS OF COBALT SOAPS ($T$=297°K)

| | $\chi_H \cdot 10^6$ | | $\chi_\infty \cdot 10^6$ | w | $\chi \cdot 10^6$ | $\chi_M \cdot 10^6$ | $\sum\chi_{dia} 10^6$ | $\chi_{para} \cdot 10^6$ | $\mu$ |
|---|---|---|---|---|---|---|---|---|---|
| | $H$=22500 | 16400 | (calcd.) | wt. % | | | | | BM |
| | $1/H \cdot 10^4$=0.444 | 00610 | 0 | | | | | | |
| Red cobalt stearate dihydrate | | | | | | ($M$=661.89) | | | |
| | 3.16 | 3.37 | $2.59_5$ | | | | | | |
| | 3.07 | 3.27 | $2.53_5$ | | | | | | |
| | | | Av. 2.57 | 19.8 | $14.0_4$ | 9286.3 | −456 | 8830.3 | $4.59_7$ |
| Blue cobalt stearate anhydrate | | | | | | ($M$=625.86) | | | |
| | 2.48 | 3.57 | $2.23_9$ | | | | | | |
| | 2.51 | 2.61 | $2.24_2$ | | | | | | |
| | | | Av. 2.24 | 18.8 | $13.0_3$ | 8155.0 | −430 | 7725.0 | $4.30_0$ |

TABLE V. ELECTRONIC CONFIGURATIONS OF COBALT(II) COMPLEXES[9,10]

| Type | Coordination number | Geometry of complex | Electronic configurations (3d 4s 4p 4d 5s) | Hybrid orbitals | Observed magnetic moment $\mu_{eff}$, BM |
|---|---|---|---|---|---|
| Free $Co^{2+}$ ion | | | ↑↓ ↑ ↑ ↑ ↑ ↑ | | |
| Spin-free or ionic covalent | 6 | octahedral | ↑↓ ↑ ↑ ↑ ↑ ↑ × × × × × × | $(4s)(4p)^3(4d)^2$ | 4.9～5.6 |
| | 4 | tetrahedral | ↑↓ ↑ ↑ ↑ ↑ ↑ × × × × | $(4s)(4p)^3$ | 4.3～4.8 |
| | 4 | square, planar | ↑↓ ↑ ↑ ↑ ↑ ↑ × × × × | $(4s)(4p)^2(4d)$ | 4.8～5.4 |
| Spin-paired covalent | 4 | square, planar | ↑↓ ↑↓ ↑ ↑ × × × × | $(3d)(4s)(4p)^2$ | 2.1～2.9 |
| | 6 | presumably tetragonal (a) | ↑↓ ↑↓ ↑ ↑ × × × × × × | $(3d)(4s)(4p)^3(4d)$ | 1.7～2.0 |
| | | (b)* | ↑↓ ↑↓ ↑ ↑ × × × × ↑ | $(3d)^2(4s)(4p)^3$ | |

×× : Bonding orbitals.
* Figgis and Nyholm[9] proposed originally this configuration, but considered later that this improbable.

free water. Therefore, it was concluded that water in cobalt soaps exists as hydration water.

**Magnetic Susceptibilities.** — Observed values of magnetic susceptibilities and magnetic moments, calculated as stated above, of red and blue cobalt stearates are shown in Table IV.

Figgis and Nyholm[9] have shown that, according to magnetic moment, cobalt(II) compounds may be classified into two types, that is, the spin-free or ionic covalent type and the spin-paired covalent type, as shown in Table V. The number of unpaired electrons, $n$, in these configurations is three and one. Therefore, the spin only value of magnetic moment, $\mu_{eff}=\sqrt{n(n+2)}$, is 3.88 and 1.73 BM, respectively. The observed values of many complexes of each type were 4.2～5.6 BM in the spin-free type, and 1.7～2.9 BM in the spin-paired type, as shown in Table V.

On the basis of these facts it has been concluded that the cobalt soaps used in the present paper were spin-free or ionic covalent complexes. This conclusion is completely consistent with the results of infrared absorption measurements.

Observed values of magnetic moments of cobalt(II) complexes are generally larger than spin only values, for the contribution of the orbital motion of electrons was not completely quenched in them owing to the presence of ligand fields and spin-orbit couping. Among ionic covalent complexes, the orbital contribution is smaller in tetrahedral $sp^3$ orbitals than in octahedral $sp^3d^2$ orbitals. This is based on the difference of multiplicities of ground states in these configurations[10].

Although our values are somewhat smaller than that of Figgis and Nyholm, blue and red cobalt soaps must correspond to the $(4s)(4p)^3$ tetrahedral four-covalent complex and the $(4s)(4p)^3(4d)^2$ octahedral six-covalent complex respectively. Holm and Cotton[10] have proposed the $(4s)(4p)^2(4d)$ square planar, ionic covalent type for some cobalt(II) complexes, but this configuration may be excluded from our cases by considerations of color.

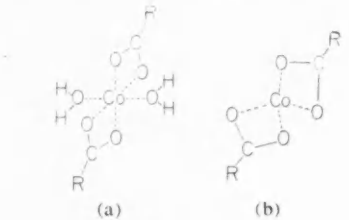
9) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1954**, 12; **1959**, 331, 338.

10) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959); **32**, 1168 (1960); *J. Am. Chem. Soc.*, **82**, 2979, 2983 (1960).

The magnetic moments of rose-pink cobalt laurate dihydrate and purple anhydrate of cobalt stearate and laurate obtained by Herron and Pink[5] were larger than our values, as has been shown before. In contrast with our results, they found no difference in magnetic moments between anhydrate and dihydrate of cobalt laurate. As their purple anhydrate was prepared by boiling rose-pink dihydrate with solvent, it might be a glassy form recovered from a molten state. In our experiments, which will be discussed in a later part of these studies, a once-melted soap showed a somewhat larger magnetic moment than a true blue form. The orbital contribution is so much affected by a crystal field[10] that the melted form must have a different contribution of orbital motion to the magnetic moment.

Moreau and Vatteroni[9] compared the magnetic susceptibilities of cobalt soaps with that of cobalt sulfate and found that the values of cobalt soaps were somewhat larger than inorganic salt. They concluded that these soaps were regarded as structure complexes. This is also consistent with our results.

**Structure Formulas of Cobalt Soaps.**—From these results, it may be concluded that red dihydrate and blue anhydrate of cobalt stearate have a geometry of octahedral and tetrahedral coordination complex respectively. The structure formulas of these soaps may be described as shown in Fig. 4, following Herron and Pink[5]. Such a formula was proposed for cupric salts of lower fatty acids by French and Lowry[11] and opposed by Sidgwick[12]. Sidgwick's main reason for rejecting this formula was that the strain in the chelate ring of four members makes them exceedingly unstable. The alternative formula, in which the carboxyl group occupies two coordination positions attaching themselves to two different cobalt ions, so as to form a ring of more than four members, must be proposed. This was done in cupric soaps[5], but not yet for cobalt soaps.




(a) (b)

Fig. 4. Proposed structure formulas of cobalt soaps.
(a) Red dihydrate (b) Blue anhydrate

## Summary

The infrared absorption spectra and the magnetic susceptibilities of red dihydrate and blue anhydrate of cobalt stearate were measured. The infrared spectra showed the existence of carboxylate ion in these soaps, and magnetic measurements confirmed that they are ionic in nature.

The magnetic moments of red and blue cobalt stearates showed that they are spin-free or ionic covalent complexes. The geometry of red soap is six-covalent octahedral, and that of blue is four-covalent tetrahedral. Structure formulas were proposed for them in correspondence with these geometries, but they may be improbable because of the existence of unstable rings of four members. Alternative formulas, in which a carboxyl group joins two cobalt ions, might be considered but have not yet been given.

The authors express their gratitude to Professor Bunnosuke Yamaguchi for his advice throughout this work, and to Dr. Yoshio Matsunaga and Mr. Shiro Morita for their accomplishments in magnetic and some infrared absorption measurements.

*Institute for Science and Technology*
*The University of Tokyo*
*Meguro-ku, Tokyo*

11) H. S. French and T. M. Lowry, *Proc. Roy. Soc.*, **106A**, 489 (1924).
12) N. V. Sidgwick, "The Electronic Theory of Valency", Oxford Univ. Press, Oxford (1927), p. 252.

# *Statistical Thermodynamics of Solutions of Optically Active Substances. II. Solubility of d- and l-Isomers in Optically Active Solvents*

By Kazuo AMAYA

(Received March 1, 1961)

It is expected theoretically that when *d*- and *l*-optical isomers are independently dissolved in an optically active liquid, the solubilities of *d*- and *l*-isomers may be different. To elucidate the special feature of this problem, the theoretical expression for the solubilities of *d*- and *l*-optical isomers is based on the model described in a previous paper[1]. Further a possibility of optical resolution is discussed.

## Theory

Let us consider two kinds of systems, the one of which contains optically active liquid substance A and *l*-isomer of optically active molecule B (which is denoted by $B_l$) and the other contains A and *d*-isomer of optically active molecule B (which is denoted by $B_d$). For simplicity it is assumed that the two components are completely immiscible in the solid state and completely miscible in the liquid state.

The chemical potential of $B_l$ molecule in crystal $\mu^{K}_{B_l}$ is a function of absolute temperature, $T$, alone while the chemical potential of the same molecule in solution $\mu^{S}_{B_l}$ is a function of, $T$, mole fraction of $B_l$, $x_{B_l}$, and interaction parameter between A and $B_l$ molecules, $\omega_{AB_l}$. For a saturated solution of $B_l$ in A the chemical potential of $B_l$ is equal to that in the crystal, then it follows that

$$\mu^{K}_{B_l}(T) = \mu^{S}_{B_l}(T, x_{B_l}, \omega_{AB_l}) \qquad (1)$$

In a similar way for a saturated solution of $B_d$ in the following expression is obtained

$$\mu^{K}_{B_d}(T) = \mu^{S}_{B_d}(T, x_{B_d}, \omega_{AB_d}) \qquad (2)$$

where $\mu^{K}_{B_d}$ and $\mu^{S}_{B_d}$ are the chemical potentials of $B_d$ molecule in the crystal and in the saturated solution respectively, and $x_{B_d}$ is the mole fraction of $B_d$ in the solution and $\omega_{AB_d}$ is an interaction parameter between A and $B_d$ molecules.

As $B_l$ and $B_d$ molecules are mirror images for each other, the chemical potential of $B_l$ molecule is equal to that of $B_d$ molecule in the crystal at the same temperature. Then it follows from 1 and 2 that

$$\mu^{K}_{B_l}(T) = \mu^{K}_{B_d}(T) = \mu^{S}_{B_l}(T, x_{B_l}, \omega_{AB_l}) = \mu^{S}_{B_d}(T, x_{B_d}, \omega_{AB_d}) \qquad (3)$$

Since $\omega_{AB_l}$ and $\omega_{AB_d}$ have different values, $x_{B_l}$ and $x_{B_d}$ in each saturated solution have different values. It means that the solubility of $B_d$ and $B_l$ optical isomers differ from each other. In the following, explicit expressions for $\mu^{S}_{B_l}$ and $\mu^{S}_{B_d}$ will be derived. In deriving the theoretical expressions, the following assumptions are made:

(1) Molecule A, $B_l$ and $B_d$ are equal in size and each occupies a site of quasi-crystalline lattice and has $3z$ orientational freedoms.

(2) Molecule A is covered by $z$ planes, one of which is composed of $a$ element, and the others $(z-1)$ are composed of $b$ elements. The $a$ element is composed of three subelements 1, 2 and 3 and their arrangement is in the order 1, 2, 3 clockwise viewed from outside of the molecule.

(3) Molecule B (both $B_l$ and $B_d$) is also covered by $z$ planes, one of which is composed of $a'$ element and the others $(z-1)$ are composed of $b'$ elements. $a'$ element is composed of three subelements $1'$, $2'$ and $3'$ and their arrangement is in the order $1'$, $2'$, $3'$ clockwise for $B_l$ molecule and $1'$, $3'$, $2'$ clockwise for $B_d$ molecule viewed from outside of the molecule.

(4) The configurational energy of the system is the sum of interaction energies of plane-plane pairs.

If the interaction energy of plane $i$ and plane $j$ is denoted by $\omega_{ij}$, all possible kinds of $\omega_{ij}$ and their interaction energies become as follows.

A−A $\quad \omega_{bb}, \omega_{ab}, \omega_{aa_1} = \omega_{11} + 2\omega_{23}$

$\omega_{aa_2} = \omega_{22} + 2\omega_{13}$

$\omega_{aa_3} = \omega_{33} + 2\omega_{12}$

B−$B_l$, B−$B_d$ $\quad \omega_{b'b'}, \omega_{a'b'}, \omega_{a'a'_1} = \omega_{1'1'} + 2\omega_{2'3'}$

$\omega_{a'a'_2} = \omega_{2'2'} + 2\omega_{1'3'}$

$\omega_{a'a'_3} = \omega_{3'3'} + 2\omega_{1'2'}$

A−$B_l$ $\quad \omega_{bb'}, \omega_{ab'}, \omega_{aa'_1}, \omega^{l}_{aa_1} = \omega_{11'} + \omega_{23'} + \omega_{32'}$

$\omega^{l}_{aa'_2} = \omega_{22'} + \omega_{13'} + \omega_{31'}$

$\omega^{l}_{aa'_3} = \omega_{33'} + \omega_{12'} + \omega_{21'}$

1) K. Amaya, This Bulletin, 34, 1689 (1961).

$\mathrm{A}-\mathrm{B}_l$ $\omega_{bb'}, \omega_{ab'}, \omega_{a'b}, \omega^{\mathrm{I}}_{aa'_1}=\omega_{11'}+\omega_{22'}+\omega_{33'}$

$\omega^{\mathrm{I}}_{aa'_2}=\omega_{13'}+\omega_{21'}+\omega_{32'}$

$\omega^{\mathrm{I}}_{aa'_3}=\omega_{12'}+\omega_{23'}+\omega_{31'}$.

The total configurational energy of the system is expressed as a sum of these energies. For a system composed of $N_\mathrm{A}$ molecules of A and $N_{\mathrm{B}l}$ molecules of $\mathrm{B}_l$, the configurational partition function $\Omega_{\mathrm{AB}l}$ is given by

$$\ln \Omega_{\mathrm{AB}l}-\ln\frac{(N_\mathrm{A}+N_{\mathrm{B}l})!}{N_\mathrm{A}!\,N_{\mathrm{B}l}!}-\ln(3z)^{N_\mathrm{A}+N_{\mathrm{B}l}}-\frac{N_\mathrm{A}\chi_\mathrm{A}+N_{\mathrm{B}l}\chi_{\mathrm{B}l}}{kT}=\frac{\langle W_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle}{kT}-\frac{\langle W_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle^2-\langle W^2_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle}{2!\,(kT)^2}-\cdots\cdots \tag{4}$$

where

$$\chi_\mathrm{A}=\frac{z}{2}\cdot\frac{1}{z^2}\left\{(z-1)^2\omega_{bb}+2(z-1)\omega_{ab}+\frac{1}{3}(\omega_{aa_1}+\omega_{aa_2}+\omega_{aa_3})\right\} \tag{5}$$

$$\chi_\mathrm{B}=\frac{z}{2}\cdot\frac{1}{z^2}\left\{(z-1)^2\omega_{b'b'}+2(z-1)\omega_{a'b'}+\frac{1}{3}(\omega_{a'a'_1}+\omega_{a'a'_2}+\omega_{a'a'_3})\right\} \tag{6}$$

and $W_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})$ is the excess potential energy of the system and $\langle W_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle$ and $\langle W_{\mathrm{AB}l}{}^2(N_\mathrm{A},N_{\mathrm{B}l})\rangle$ denote the unweighted mean over all configurations of this quantity and of the square of it respectively. Then $\langle W_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle$ is given by

$$\langle W_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle=(N_\mathrm{A}+N_{\mathrm{B}l})\{(1-x_{\mathrm{B}l})^2\chi_\mathrm{A}+2x_{\mathrm{B}l}(1-x_{\mathrm{B}l})\chi_{\mathrm{AB}l}+x^2{}_{\mathrm{B}l}\chi_{\mathrm{B}l}\}-N_\mathrm{A}\chi_\mathrm{A}-N_{\mathrm{B}l}\chi_{\mathrm{B}l}$$

$$=(N_\mathrm{A}+N_{\mathrm{B}l})x_{\mathrm{B}l}(1-x_{\mathrm{B}l})(2\chi_{\mathrm{AB}l}-\chi_\mathrm{A}-\chi_{\mathrm{B}l})^* \tag{7}$$

where

$$x_{\mathrm{B}l}=N_{\mathrm{B}l}/(N_\mathrm{A}+N_{\mathrm{B}l})$$

$$\chi_{\mathrm{AB}l}=\frac{1}{z}\left\{(z-1)^2\omega_{bb'}+(z-1)(\omega_{ab'}+\omega_{a'b})+\frac{1}{3}(\omega^l_{aa'_1}+\omega^l_{aa'_2}+\omega^l_{aa'_3})\right\}$$

In evaluating $\langle W^2{}_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle$, the average value over most probable configurations is taken as an approximation, since it is very difficult to evaluate the exact value of this quantity averaged over all possible configurations. For most probable configurations, the number of plane-plane pairs for each kind of pair becomes as shown in Table I.

The average value over the above configurations becomes as follows with a procedure similar to that described in the previous paper[1].

$$\langle \mathrm{W}_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle^2-\langle W^2{}_{\mathrm{AB}l}(N_\mathrm{A},N_{\mathrm{B}l})\rangle=-\frac{(N_\mathrm{A}+N_{\mathrm{B}l})^2}{4z^2}\Big[(1-x_{\mathrm{B}l})^4\cdot\frac{1}{36}\{(\omega_{aa_1}-\omega_{aa_3})^2+(\omega_{aa_2}-\omega_{aa_3})^2+(\omega_{aa_2}-\omega_{aa_1})^2\}+4x^2{}_{\mathrm{B}l}(1-x_{\mathrm{B}l})^2\cdot\frac{1}{36}\{(\omega^l_{aa'_1}-\omega^l_{aa'_3})^2+(\omega^l_{aa'_2}-\omega^l_{aa'_3})^2+(\omega^l_{aa'_3}-\omega^l_{aa'_1})^2\}+x^4{}_{\mathrm{B}l}\cdot\frac{1}{36}\{(\omega_{a'a'_1}-\omega_{a'a'_2})^2+(\omega_{a'a'_2}-\omega_{a'a'_3})^2+(\omega_{a'a'_3}-\omega_{a'a'_1})^2\}\Big] \tag{8}$$

By substituting 8 into 4, the following expression for configurational partition function $\Omega_{\mathrm{AB}l}$ is obtained.

TABLE I

| | The kind of pairs | Number of pairs | |
|---|---|---|---|
| A−A | $b-b$ | $(z-1)^2/z^2\cdot N_{\mathrm{AA}}$ | |
| | $a-b$ | $2(z-1)/z^2\cdot N_{\mathrm{AA}}$ | $N_{\mathrm{AA}}=\frac{1}{2}(N_\mathrm{A}+N_{\mathrm{B}l})z(1-x_{\mathrm{B}l})^2$ |
| | $a-a$ | $1/z^2\cdot N_{\mathrm{AA}}$ | |
| $\mathrm{B}_l-\mathrm{B}_l$ | $a'-b'$ | $(-1)^2/z^2\cdot N_{\mathrm{B}l\mathrm{B}l}$ | |
| | $a'-b'$ | $2(z-1)/z^2\cdot N_{\mathrm{B}l\mathrm{B}l}$ | $N_{\mathrm{B}l\mathrm{B}l}=\frac{1}{2}(N_\mathrm{A}+N_{\mathrm{B}l})zx^2{}_{\mathrm{B}l}$ |
| | $a'-a'$ | $1/z^2\cdot N_{\mathrm{B}l\mathrm{B}l}$ | |
| A−$\mathrm{B}_l$ | $b-b'$ | $(z-1)^2/z^2\cdot N_{\mathrm{AB}l}$ | |
| | $a-b'$ | $(z-1)/z^2\cdot N_{\mathrm{AB}l}$ | $N_{\mathrm{AB}l}=(N_\mathrm{A}+N_{\mathrm{B}l})z\cdot x_{\mathrm{B}l}(1-x_{\mathrm{B}l})$ |
| | $a'-b$ | $(z-1)/z^2\cdot N_{\mathrm{AB}l}$ | |
| | $a-a'$ | $1/z^2\cdot N_{\mathrm{AB}l}$ | |

* Mean cohesive energy of a B molecule in an imagi- nary liquid state.

$$\ln \Omega_{AB_l}=\ln \frac{(N_A+N_{B_l})!}{N_A!\,N_{B_l}!}+\ln(3z)^{N_A+N_{B_l}}+\frac{N_A\chi_A+N_{B_l}\chi_{B_l}}{kT}-\frac{(N_A+N_{B_l})}{kT}(2\chi_{AB_l}-\chi_A-\chi_{B_l})x_{B_l}(1-x_{B_l})+\frac{1}{2(kT)^2}\frac{(N_A+N_{B_l})^2}{4z^2}\Big[(1-x_{B_l})^4\cdot\frac{1}{36}\{(\omega_{aa_1}-\omega_{aa_3})^2+(\omega_{aa_2}-\omega_{aa_3})^2+(\omega_{aa_3}-\omega_{aa_1})^2\}+4x^2_{B_l}(1-x_{B_l})^2\cdot\frac{1}{36}\{(\omega^l_{a'a'_1}-\omega^l_{a'a'_2})^2+(\omega^l_{a'a'_2}-\omega^l_{a'a'_3})^2+(\omega^l_{a'a'_3}-\omega^l_{a'a'_1})^2\}+x^4_{B_l}\cdot\frac{1}{36}\{(\omega_{a'a'_1}-\omega_{a'a'_2})^2+(\omega_{a'a'_2}-\omega_{a'a'_3})^2+(\omega_{a'a'_3}-\omega_{a'a'_1})^2\}\Big] \tag{9}$$

Then the chemical potential of $B_l$ molecules $\mu^S_{B_l}$ can be obtained by partial differentiating $-kT\ln\Omega_{AB_l}$ with respect to $N_{B_l}$

$$\mu^S_{B_l}=-\frac{\partial kT\ln\Omega_{AB_l}}{\partial N_{B_l}}=kT\ln x_{B_l}-\chi_{B_l}+(1-x_{B_l})^2(2\chi_{AB_l}-\chi_A-\chi_{B_l})-\frac{1}{36}\frac{N}{z^2}\frac{1}{kT}\Big[-(1-x_{B_l})^4\{(\omega_{aa_1}-\omega_{aa_2})^2+(\omega_{aa_2}-\omega_{aa_3})^2+(\omega_{aa_3}-\omega_{aa_1})^2\}+x_{B_l}(1-x_{B_l})^3\{(\omega^l_{a'a'_1}-\omega^l_{a'a'_2})^2+(\omega^l_{a'a'_2}-\omega^l_{a'a'_3})^2+(\omega^l_{a'a'_3}-\omega^l_{a'a'_1})^2\}+x^2_{B_l}(2-x_{B_l})\{(\omega_{a'a'_1}-\omega_{a'a'_2})^2+(\omega_{a'a'_2}-\omega_{a'a'_3})^2+(\omega_{a'a'_3}-\omega_{a'a'_1})^2\}\Big] \tag{10}$$

where $N=N_A+N_{B_l}$.

For the system consisting of $N_A$ molecules of A and $N_{B_d}$ molecules of $B_d$, the chemical potential $\mu^S_{B_d}$ for the $B_d$ molecule can be derived in quite the same way. Then $\mu^S_{B_d}$ becomes

$$\mu^S_{B_d}=kT\ln x_{dB}-\chi_{B_d}+(1-x_{B_d})^2(2\chi_{AB_d}-\chi_A-\chi_{B_d})-\frac{1}{36}\frac{N}{z^2}\frac{1}{kT}\Big[-(1-x_{B_d})^4\{(\omega_{aa_1}-\omega_{aa_2})^2+(\omega_{aa_2}-\omega_{aa_3})^2+(\omega_{aa_3}-\omega_{aa_1})^2\}+x_{B_d}(1-x_{B_d})^3\{(\omega^d_{a'a'_1}-\omega^d_{a'a'_2})^2+(\omega^d_{a'a'_2}-\omega^d_{a'a'_3})^2+(\omega^d_{a'a'_3}-\omega^d_{a'a'_1})^2\}+x^2_{B_d}(2-x_{B_d})\{(\omega_{a'a'_1}-\omega_{a'a'_2})^2+(\omega_{a'a'_2}-\omega_{a'a'_3})^2+(\omega_{a'a'_3}-\omega_{a'a'_1})^2\}\Big] \tag{11}$$

where

$$\chi_{AB_d}=\frac{1}{z}\Big\{(z-1)^2\omega_{bb'}+(z-1)(\omega_{ab'}+\omega_{a'b})+\frac{1}{3}(\omega^d_{a'a'_1}+\omega^d_{a'a'_2}+\omega^d_{a'a'_3})\Big\} \tag{12}$$

Now compare 10 with 11. Since $B_l$ is a mirror image of $B_d$ and $B_l$ molecules are energetically equivalent, it follows that

$$\chi_{B_l}=\chi_{B_d} \tag{13}$$

and from the relation

$$\begin{aligned}\omega^l_{a'a'_1}+\omega^l_{a'a'_2}+\omega^l_{a'a'_3}&=\omega_{11'}+\omega_{23'}+\omega_{32'}+\omega_{22'}+\omega_{13'}+\omega_{31'}+\omega_{33'}+\omega_{12'}+\omega_{21'}\\&=\omega_{11'}+\omega_{22'}+\omega_{23'}+\omega_{13'}+\omega_{21'}+\omega_{32'}+\omega_{12'}+\omega_{23'}+\omega_{31'}\\&=\omega^d_{a'a'_1}+\omega^d_{a'a'_2}+\omega^d_{a'a'_3}\end{aligned}$$

it follows that

$$\chi_{AB_l}=\chi_{AB_d} \tag{14}$$

Then the only difference between 10 and 11 is the second term in the bracket [ ] which contain the coefficient $x_B(1-x_B)^3$ *.

By using new notations that $\chi_B=\chi_{B_l}=\chi_{B_d}$ and $\chi_{AB}=\chi_{AB_l}=\chi_{AB_d}$, and expressing mole fractions of $B_l$ and $B_d$ molecules in their saturated solutions by $x_l$, and $x_d$ respectively, $x_l$ and $x_d$ are correlated by the following equations

$$\mu^S_{B_l}(x_l)=kT\ln x_l-\chi_B+(1-x_l)^2(2\chi_{AB}-\chi_A-\chi_B)-\frac{1}{36}\frac{N}{z^2}\frac{1}{kT}\{-(1-x_l)^4C_{AA}+x_l(1-x_l)^3C_{AB_l}+x_l^3(2-x_l)C_{BB}\} \tag{15}$$

$$\mu^S_{B_d}(x_d)=kT\ln x_d-\chi_B+(1-x_d)^2(2\chi_{AB}-\chi_A-\chi_B)-\frac{1}{36}\frac{N}{z^2}\frac{1}{kT}\{-(1-x_d)^4C_{AA}+x_d(1-x_d)^3C_{AB_d}+x_d^3(2-x_d)C_{BB}\} \tag{16}$$

where

$$C_{AA}=(\omega_{aa_1}-\omega_{aa_2})^2+(\omega_{aa_2}-\omega_{aa_3})^2+(\omega_{aa_3}-\omega_{aa_1})^2$$

$$C_{BB}=(\omega_{a'a'_1}-\omega_{a'a'_2})^2+(\omega_{a'a'_2}-\omega_{a'a'_3})^2+(\omega_{a'a'_3}-\omega_{a'a'_1})^2$$

$$C_{AB_l}=(\omega^l_{aa'_1}-\omega^l_{aa'_2})^2+(\alpha^l_{aa'_2}-\omega^l_{aa'_3})^2+(\omega^l_{aa'_3}-\omega^l_{aa'_1})^2$$

$$C_{AB_d}=(\omega^d_{aa'_1}-\omega^d_{aa'_2})^2+(\omega^d_{aa'_2}-\omega^d_{aa'_3})^2+(\omega^d_{aa'_3}-\omega^d_{aa'_1})^2$$

* $x_B$ denotes $\chi_{B_l}$ or $\chi_{B_d}$.

## Discussions

The chemical potentials of $B_l$ and $B_d$ molecules in the solution $\mu^{S}_{B_l}(x)$ and $\mu^{S}_{B_d}(x)$ respectively, can be expressed as a function of their mole fraction $x$ by the same formula except for the term containing $C_{AB_l}$ and $C_{AB_d}$. If the common part is expressed by $F(x)$, the following formula is obtained.

$$\mu^{S}_{B_l}(x) = F(x) + \frac{1}{36}\frac{N}{z^2}\frac{1}{kT} C_{AB_l} x(1-x)^3 + \cdots\cdots$$

$$\mu^{S}_{B_d}(x) = F(x) + \frac{1}{36}\frac{N}{z^2}\frac{1}{kT} C_{AB_d} x(1-x)^3 + \cdots\cdots$$

This formula is represented schematically in Fig. 1. It is clear from the above expression that the higher the temperature the greater the difference between the two curves is. The straight line parallel to the $x$ axis representing $\mu = \mu^{K}$ crosses the curves representing $\mu^{S}_{B_l}(x)$ and $\mu^{S}_{B_d}(x)$ at points $P_l$ and $P_d$. Projections of $P_l$ and $P_d$ on $x$ axis represent $x_l$ and $x_d$ respectively. As these two curves generally do not coincide with each other, $x_l$ and $x_d$ have different values. This shows that the solubilities of *d*- and *l*-optical isomers in optical active solvent differ from each other and the magnitude of the difference is determined by the difference between $C_{AB_l}$ and $C_{AB_d}$. It is clear from the above argument that in principle the optical resolution is possible using the difference of solubility of *d*- and *l*-optical isomers in optical active solvents and by choosing a proper kind of molecule of A, which makes the difference of $C_{AB_l}$ and $C_{AB_d}$ large, the difference between $x_l$ and $x_d$ can be made large enough to obtain an efficient optical resolution.

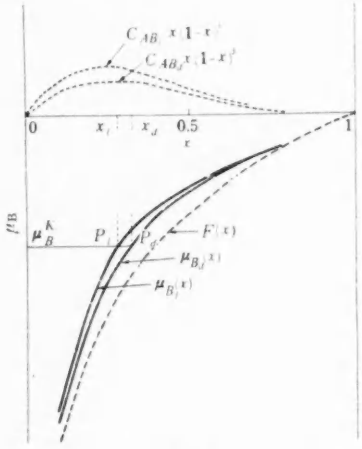



Fig. 1. Schematic diagram of $\mu_{B_l}$ and $\mu_{B_d}$ as a function of $x$.

The above argument is confined only to the mixture in which $B_l$ and $B_d$ molecules form no racemic compound. For the case where a racemic compound is formed more elaborate consideration must be made.

## Summary

The statistical mechanical expression relating the solubilities of *d*- and *l*-optical isomers in optically active solvent is derived.

It is shown that there exists a difference between these two solubilities.

The possibility of optical resolution is also discussed.

The auther wishes to express his hearty thanks to Professor Yonezo Morino of The University of Tokyo for his helpful discussions.

*Government Chemical*
*Industrial Research Institute*
*Shibuya-ku, Tokyo*

# *Liquid-Vapor Equilibrium of Isotope Mixture under Centrifugal Force*

By Kazuo AMAYA

(Received March 30, 1961)

In order to estimate the efficiency of concentrating one of the isotopic compounds by distillation of the mixture under centrifugal force, a theoretical expression for liquid-vapor equilibrium of the isotopic mixture under centrifugal force was derived and a concentration factor under practical condition was estimated for actual cases.

## Derivation of the Expression for the Distribution of Isotope Mixture in Liquid-Vapor Phase System under Centrifugal Force

Consider an isotopic mixture composed of $N_1$ molecules of isotope 1 of mass $m_1$ and $N_2$ molecules of isotope 2 of mass $m_2$.

If the mole fraction of isotope 1 in the mixture is denoted by $x$, then

$$N_1 = Nx \tag{1}$$

$$N_2 = N(1-x) \tag{2}$$

where $N = N_1 + N_2$.

Suppose that the mixture is confined in a closed box with cross section area $S$ and height $H$ and is placed in a field of homogeneous centrifugal force $g$*, the direction of which is perpendicular to the cross section.

If the densities of molecules of isotope 1 and 2 in the vapor phase at a distance $h^v$ from the liquid surface are denoted by $n^v_{1g}(h^v)$ and $n^v_{2g}(h^v)$ respectively and those in the liquid phase by $n^l_{1g}(h^l)$ and $n^l_{2g}(h^l)$ respectively, and suppose that the vapor density is sufficiently low and the liquid is not compressible, then following relations hold.

$$n^v_{1g}(h^v) = n^v_{1g}(0)\cdot\exp(-m_1gh^v/\boldsymbol{kT}) \tag{3}$$

$$n^v_{2g}(h^v) = n^v_{2g}(0)\cdot\exp(-m_2gh^v/\boldsymbol{kT}) \tag{4}$$

$$n^l_{1g}(h^l) + n^l_{2g}(h^l) = n^l_{1g}(0) + n^l_{2g}(0) = N_0 = \text{const.} \tag{5}$$

$$n^l_{1g}(h^l) = N_0\cdot n^l_{1g}(0)\cdot\exp(m_1gh^l/\boldsymbol{kT})/\{n^l_{1g}(0)\cdot\exp(m_1gh^l/\boldsymbol{kT}) + n^l_{2g}(0)\cdot\exp(m_2gh^l/\boldsymbol{kT})\} \tag{6}$$

$$n^l_{2g}(h^l) = N_0\cdot n^l_{2g}(0)\cdot\exp(m_2gh^l/\boldsymbol{kT})/\{(n^l_{1g}(0)\cdot\exp(m_1gh^l/\boldsymbol{kT}) + n^l_{2g}(0)\cdot\exp(m_2gh^l/\boldsymbol{kT})\} \tag{7}$$

where $\boldsymbol{k}$ is the Boltzmann constant and $\boldsymbol{T}$ is the absolute temperature of the box.

If the vaporization energy of isotope 1 is assumed to be equal to that of isotope 2, then it follows that,

$$n^l_{1g}(0) = K_T n^v_{1g}(0) \tag{8}$$

$$n^l_{2g}(0) = K_T n^v_{2g}(0) \tag{9}$$

where $K_T$ is a constant at a given temperature, $T$. From the principle of conservation of mass in a closed system, the following relations are obtained.

$$S\int_0^{H^v_g} n^v_{1g}(h^v)\mathrm{d}h_v + S\int_0^{H^l_g} n^l_{1g}(h^l)\mathrm{d}h_l = Nx \tag{10}$$

$$S\int_0^{H^v_g} n^v_{2g}(h^v)\mathrm{d}h_v + S\int_0^{H^l_g} n^l_{2g}(h^l)\mathrm{d}h_l = N(1-x) \tag{11}$$

where $SH^v_g$ and $SH^l_g$ are the volume of the space in the box occupied by the vapor and the liquid respectively at equilibrium under centrifugal force $g$ and namely $H = H^v_g + H^l_g$.

If, at equilibrium, mole fraction of isotope at the interface of liquid and vapor is denoted by $x_g$ it follows from 5 that

$$n^l_{1g}(0) = N_0 x_g \tag{12}$$

$$n^l_{2g}(0) = N_0(1-x_g) \tag{13}$$

then Eqs. 6 and 7 are rewritten as

$$n^l_{1g}(h^l) = N_0 x_g\cdot\exp(m_1gh^l/\boldsymbol{kT})/\{x_g\cdot\exp(m_1gh^l/\boldsymbol{kT}) + (1-x_g)\cdot\exp(m_2gh^l/\boldsymbol{kT})\} = N_0\left/\left[1+\frac{1-x_g}{x_g}\cdot\exp\{(m_2-m_1)gh^l/\boldsymbol{kT}\}\right]\right. \tag{14}$$

$$n^l_{2g}(h^l) = N_0(1-x_g)\cdot\exp(m_2gh^l/\boldsymbol{kT})/\{x_g\cdot\exp(m_1gh^l/\boldsymbol{kT}) + (1-x_g)\cdot\exp(m_2gh^l/\boldsymbol{kT})\} = N_0\left/\left[1+\frac{x_g}{1-x_g}\cdot\exp\{(m_1-m_2)gh^l/\boldsymbol{kT}\}\right]\right. \tag{15}$$

and from 3, 4, 8 and 9

* For the sake of simplicity, the values of $g$ are assumed to be constant along the direction of height.

$$n^{v}_{1g}(h^{v}) = N_0/K_T \cdot x_g \cdot \exp(-m_1 g h^{v}/\boldsymbol{kT}) \quad (16)$$

$$n^{v}_{2g}(h^{v}) = N_0/K_T \cdot x_g \cdot \exp(-m_2 g h^{v}/\boldsymbol{kT}) \quad (17)$$

Substituting 14 and 16 into 10, and 15 and 17 into 11, and integrating them, we obtain

$$Nx = N_0 S\Big[ x_g/K_T \cdot \boldsymbol{kT}/m_1 g\{1-\exp(-m_1 g H^{v}_g/\boldsymbol{kT})\} + H^{l}_g - \boldsymbol{kT}/(m_2-m_1)g \times \ln\Big\{\frac{1+(1-x_g)/x_g \cdot \exp((m_2-m_1)gH^{l}_g/\boldsymbol{kT})}{1+(1-x_g)/x_g}\Big\}\Big] \quad (18)$$

$$N(1-x) = N_0 S\Big[ (1-x_g)/K_T \cdot \boldsymbol{kT}/m_2 g\{1-\exp(-m_2 g H^{v}_g/\boldsymbol{kT})\} + H^{l}_g - \boldsymbol{kT}/(m_1-m_2)g \times \ln\Big\{\frac{1+x_g/(1-x_g)\cdot\exp((m_1-m_2(gH^{l}_g/\boldsymbol{kT})}{1+x_g/(1-x_g)}\Big\}\Big] \quad (19)$$

### Calculation of Concentration Factor for Actual Cases

Now, the change of composition of isotope in the mixture by distillation under centrifugal force will be considered. When $g=0$, Eqs. 18 and 19 become

$$Nx = N_0 S x_0 (1/K_T \cdot H^{v}_0 + H^{l}_0) \quad (20)$$

$$N(1-x) = N_0 S(1-x_0)(1/K_T \cdot H^{v}_0 + H^{l}_0) \quad (21)$$

where $H^{v}_0$, $H^{l}_0$ and $x_0$* are the values of $H^{v}_g$, $H^{l}_g$ and $x_g$ when $g=0$ respectively. By Eqs. 18 and 19 to 20 and 21 respectively and from the relation

$$H^{l}_0 + H^{v}_0 = H^{l}_g + H^{v}_g \quad (22)$$

the values of $x_g/x_0$ may be obtained in principle. However, the exact solution of these equations is very complicated.

In order to obtain a workable formula, we may expand the logarithm of the last terms in 18 and 19 in powers of $(m_2-m_1)gH^{l}_g/\boldsymbol{kT}$, and the following relations are obtained

$$x_g/K_T \cdot [\boldsymbol{kT}/m_1 g \cdot \{1-\exp(-m_1 g H^{v}_g/\boldsymbol{kT})\} + H^{l}_g] + 1/2 \cdot \{(1-x_g) - (1-x_g)^2\}(m_1-m_2)gH^{l}_g/\boldsymbol{kT} + \cdots\cdots = x_0(H^{v}_0/K_T + H^{l}_0) \quad (23)$$

$$(1-x_g)/K_T \cdot [\boldsymbol{kT}/m_2 g \cdot \{1-\exp(-m_2 g H^{v}_g/\boldsymbol{kT})\} + H^{l}_g] + 1/2 \cdot (x_g - x^{2}_g)(m_2-m_1)gH^{l}_g/\boldsymbol{kT} + \cdots\cdots = (1-x_0)(H^{v}_0/K_T + H^{l}_0) \quad (24)$$

If we assume that

$$|m_1-m_2| = 3,$$

$$H^{l}_g \approx 0.1 \text{ cm.}$$

$$g = 10^{7} \text{ dyn.}$$

$$T \approx 300^{\circ}\text{K}$$

then the order of magnitude of the second term of the left side of 23 or 24 is about $1/2 \cdot |m_1-m_2| \times 10^{-5} = 1.5 \times 10^{-5}$ and can be neglected as being sufficiently small. Using the following notation

$$x_g = x_0(1+\delta) \quad (25)$$

$$H^{l}_g = H^{l}_0 + \Delta h, \quad H^{v}_g = H^{v}_0 - \Delta h \quad (26)$$

and adding 23 and 24, we obtain

$$x_0(1+\delta)\boldsymbol{kT}/m_1 g \cdot [1-\exp\{-m_1 g(H^{v}_0 - \Delta h)/\boldsymbol{kT}\}] + \{1-x_0(1+\delta)\}\boldsymbol{kT}/m_2 g \times [1-\exp\{-m_2 g(H^{v}_0 - \Delta h)/\boldsymbol{kT}\}] - H^{v}_0 = -K_T \Delta h \quad (27)$$

To obtain the approximate value of $\Delta h$, the mixture may be assumed to be of single component of mass $m = m_1 x_0 + m_2(1-x_0)$, then

$$\boldsymbol{kT}/mg\{1-\exp(-mgH^{v}_0/\boldsymbol{kT}) \cdot (1+mg\Delta h/\boldsymbol{kT})\} - H^{v}_0 = -K_T \Delta h \quad (28)$$

The value of $\Delta h$ thus obtained is then substituted into 23 and 24, and we can obtain $\delta$ from the relation

$$\frac{\boldsymbol{kT}/m_1 g \cdot \{1-(1+m_1 g\Delta h/\boldsymbol{kT})\exp(-m_1 g H^{v}_0)\} + K_T(H^{l}_0 + \Delta h)}{\boldsymbol{kT}/m_2 g \cdot \{1-(1+m_2 g\Delta h/\boldsymbol{kT})\}\exp(-m_2 g H^{v}_0) + K_T(H^{l}_0 + \Delta h)} = \frac{1-x_0(1+\delta)}{(1-x_0)(1+\delta)} \quad (29)$$

Now consider the value of $\delta$ for an actual case. For example, consider $UF_6$ and assume that

$$m_1 = 350, \; m_2 = 353$$

$$K_T \fallingdotseq 300,^{*} \; g = 10^{7} \text{ dyn.}$$

$$T = 333^{\circ}\text{K}, \; H^{v}_0 + H^{l}_0 = 20 \text{ cm.}, \; H^{l}_0 = 0.1 \text{ cm.}$$

TABLE I. VALUES OF $\delta$, $x'_g$ AND THE CONCENTRATION FACTOR $(x'_g - x_0)/x_0$ AS FUNCTIONS OF ORIGINAL CONCENTRATION $x_0$ OF $^{235}UF_6$ IN $^{235}UF_6$—$^{235}UF_6$ MIXTURE WITH $g = 10^{7}$ dyn., $H = 20$ cm. AND $H^{l}_0 = 0.1$ cm.

| $x_0$ | $\delta \times 10^{-3}$ | $x'_g$ | $(x'_g - x_0)/x_0$ % |
|---|---|---|---|
| 0.01 | −0.95 | 0.010205 | 2.05 |
| 0.1 | −0.87 | 0.10186 | 1.86 |
| 0.2 | −0.77 | 0.20330 | 1.65 |
| 0.3 | −0.67 | 0.30432 | 1.44 |
| 0.4 | −0.58 | 0.40493 | 1.23 |
| 0.5 | −0.48 | 0.50513 | 1.03 |
| 0.6 | −0.39 | 0.60491 | 0.82 |
| 0.7 | −0.29 | 0.70429 | 0.61 |
| 0.8 | −0.19 | 0.80326 | 0.41 |
| 0.9 | −0.10 | 0.90183 | 0.20 |
| 1.0 | 0 | 1.0 | 0 |

* By dividing 20 by 21, it follows that $x_0 = x$

* The vapor is assumed to be an ideal gas, and the molar volume of vapor of 22.4 l. is divided by molar volume of $UF_6$ in liquid state 75.4 cc., to obtain 22.4/0.0754 = 297.

and $\delta$ are calculated for $x_0=0.01$, 0.05, 0.1 and 0.9 and are shown in Table I. Using these values of $\delta$ we can calculate the composition of the isotope mixture at the top of the box. The composition $x_g'$ thus obtained is also shown in Table I. The concentration factors $x_g'/x_0$ are about 1.02 and the concentration of the isotope may become quite efficient by the proper design of an apparatus for successive distillation.

**Summary**

Expressions for the distribution of the isotope mixture in liquid-vapor phase system under centrifugal force were derived. By the use of these expressions, the efficiency of the isotope concentration was estimated for actual cases under accessible conditions. It was found that an efficient concentration of the isotope from their mixture was possible by the proper design of an apparatus for successive distillation.

*Government Chemical Industrial Research Institute, Tokyo*
*Shibuya-ku, Tokyo*

---

# *Adsorbabilities of Diacidotetrammine Type Cobalt(III) Complex Ions on a Cation Exchanger*[1]

By Motoshichi Mori, Muraji Shibata and Kuniko Hori

(Received March 3, 1961)

Since King and Walter[2] reported the separation of the cis and trans isomers of dinitrotetramminecobalt(III) ions by ion-exchange chromatography, the same kind of study has been extensively developed in our laboratory on other isomers of the diacidoteterammine type complex, and as a result it has been found that the trans isomers were, as a general rule, eluted faster than the corresponding cis isomers[3,4]. In the present work, some supplementary experiments for confirming the above rule are attempted by using the complexes which are relatively unstable in aqueous solutions. Furthermore, the adsorbabilities of all the complexes, including the previous ones, on a cation exchanger are compared.

## Experimental

**Complexes.** — All the complexes were prepared according to the literatures[5], and their identity and purity were examined with the absorption spectra in an alcoholic aqueous solution. The complexes used were as follows: the trans-cis and cis-trans isomers of $[Co\,en(NH_3)_2Cl_2]Cl$ and the trans and cis isomers of $[Co\,en_2Cl_2]$, $[Co\,en_2Br_2]Br$ and $[Co\,en_2(NO_2)Cl]Cl$.

**Elution Methods.**—A column (1×10 cm.) which contained 5 g. of Ammberlite IR-120 (50~100 mesh) in sodium form was used, and the sample solution was prepared in concentrations ranging from 0.01 to 0.06 M depending on the solubility of the complexes. Fifteen milliliters of each sample solution was applied to the column, and then the column was eluted with 0.15 M sodium chloride ethanol-water (1 : 1) solution. The velocity of elution was 0.5 ml./min. Examination of the eluted species was made by measuring the optical density of the eluted fraction at particular wavelengths. The ethanol-water solution was used as the eluant to minimize the aquation rections of the complexes.

The measurement of the optical density was carried out with a Hitachi model EPU-2 spectrophotometer.

## Results and Discussion

The elution curve of a mixture of the isomeric $[Co\,en(NH_3)_2Cl_2]^+$ is shown in Fig. 1, in which the measurement of the optical density was performed at an absorption maximum and a minimum of the trans-cis ion (460 and 560 m$\mu$). As is seen in the figure, an elution maximum for the trans-cis ion appears in the fraction 10 and one for the cis-trans ion in the fractions 20 and 21. When only the trans-cis complex was applied to the

1) Separation of metal complex isomers by the ion-exchanger, Part III Partly presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957.

2) E. L. King and R. R. Walter, *J. Am. Chem. Soc.*, **74**, 4471 (1952).

3) M. Mori, M. Shibata and J. Azami, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nipoon Kagaku Zasshi*), **76**, 1003 (1955).

4) M. Mori, M. Shibata and M. Nanasawa, This Bulletin, **29**, 947 (1956).

5) J. C. Bailar and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940); A. Werner, *Ber.*, **34**, 1733 (1901); *Ann.* **386**, 48, 107, 111, 248 (1912).

column, the elution curve had its maximum in the fraction 9 and dropped to zero at the fraction 20. On the other hand, the cis-trans ion began to appear in the fraction 9 and showed the maximum elution at the fraction 21. It is, therefore, clear that each portion of the fractions 9—20 in Fig. 1 is, more or less, contaminated with both species.

The elution curves of *trans*- and *cis*-$[Co\,en_2NO_2Cl]^+$ are shown in Figs. 2 and 3. The maximum concentration of the trans compound is observed in the fraction 8, and that for the cis in the fractions 21 and 22. The elution of a mixture of these isomers was examined, but the elution curve is omitted because the absorption spectra of both isomers are quite similar, and hence no perceptible peak was obtained.

Figure 4 is the elution curve for *trans*-$[Co\,en_2Br_2]^+$ and shows the elution peak in the fraction 7. The experiment of the elution for the cis ion was unsuccessful because of the extremely low solubility of the complex.

The elution curve for the isomeric $[Co\,en_2Cl_2]^+$ in a mixed solution is shown in Fig. 5, where the elution maxima are in the fractions

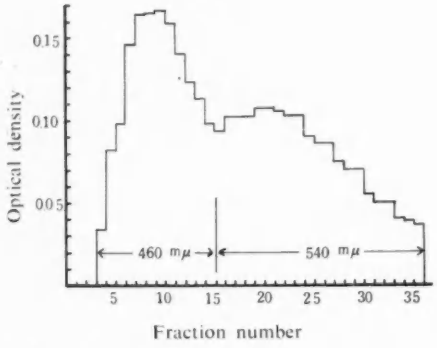



Fig. 1. Elution curve of $[Co\,en(NH_3)_2Cl_2]Cl$ isomers.

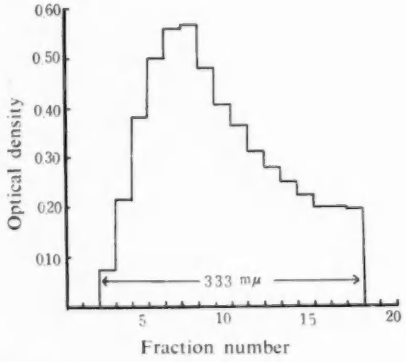



Fig. 2. Elution curve of *trans*-$[Co\,en_2NO_2Cl]Cl$.

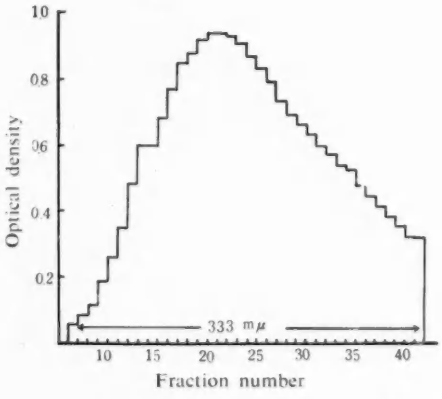



Fig. 3. Elution curve of *cis*-$[Co\,en_2NO_2Cl]Cl$.

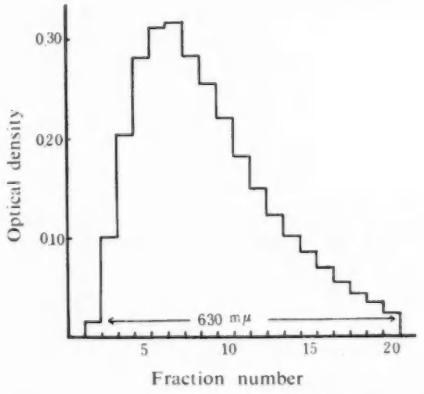



Fig. 4. Elution curve of *trans*-$[Co\,en_2Br_2]Br$.

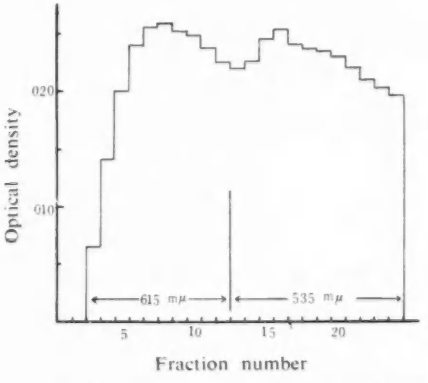



Fig. 5. Elution curve of $[Co\,en_2Cl_2]Cl$ isomers.

8 and 16. In the case of the individual solution, the trans ion was eluted with the maximum in the fraction 7 and finished its elution at the fraction 15, while the cis ion began to elute in fraction 5 and showed the maximum in the fraction 16.

From these results, it is again found that the trans ion is eluted faster than the cis ion. Furthermore, it is possible to predict the relative adsorbabilities as follows:

For the trans ions,

$$[Co\,en_2Br_2]^+ < [Co\,en_2Cl_2]^+ \simeq [Co\,en_2NO_2Cl]^+ < [Co\,en(NH_3)_2Cl_2]^+$$

For the cis ions,

$$[Co\,en_2Cl_2]^+ < [Co\,en(NH_3)_2Cl_2]^+ \simeq [Co\,en_2NO_2Cl]^+$$

Now, we are in a position to discuss the relative adsorbabilities of all the complex ions studied in the present and previous papers[3,4].

Table I. Comparison of elution maxima

| Complex ion | Eluant | Fraction no. of elution max. trans | cis |
|---|---|---|---|
| $[Co\,en(NH_3)_2Cl_2]^+$ | 0.15 M NaCl alcoholic aqueous soln. | 10 | 21—22 |
| $[Co\,en_2Cl_2]^+$ | | 8 | 16 |
| $[Co\,en_2NO_2Cl]^+$ | | 8* | 21—22* |
| $[Co\,en_2Br_2]^+$ | | 7* | — |
| $[Co\,en_2Cl_2]^+$ | 0.5 M NaCl aqueous soln. | 7 | 12 |
| $[Co\,en_2(NO_2)_2]^+$ | | 6 | 17 |
| $[Co\,en_2(NCS)_2]^+$ | | 5 | 14 |
| $[Co(NH_3)_4(NO_2)_2]^+$ | 0.5 M NaCl aqueous soln. | 13 | 35 |
| $[Co\,en_2(NO_2)_2]^+$ | | 11 | 31 |

* Fraction number in individual solution.

Unfortunately, it was impossible to perform all of the elutions under identical conditions. It is, therefore, difficult to derive a definite adsorbability order directly, but it is possible to predict such an order from a comparison of the elution maxima (Table I).

For the trans ions.

$$[Co\,en_2(NCS)_2]^+ < [Co\,en_2(NO_2)_2]^+ \simeq [Co\,en_2Br_2]^+ < [Co\,en_2Cl_2]^+ \simeq [Co\,en_2NO_2Cl]^+ < [Co(NH_3)_4(NO_2)_2]^+ < [Co\,en(NH_3)_2Cl_2]^+$$

For the cis ions.

$$[Co\,en_2Cl_2]^+ < [Co\,en_2(NCS)_2]^+ < [Co\,en(NH_3)_2Cl_2]^+ \simeq [Co\,en_2NO_2Cl]^+ < [Co\,en_2(NO_2)_2]^+ < [Co(NH_3)_4(NO_2)_2]^+$$

For the trans ions of the diacido-bisethylenediamine complexes, the adsorbabilities increase in the order of the dithiocyanato-, the dinitro-, the dibromo- and the dichloro-complexes; this trend may be attributed to the differences of the ionic radii of the complex ions since the distance between the cobalt and the ligand ion increases in the order $Cl^-$, $Br^-$, $NO_2^-$ and $NCS^-$. On the other hand, such a trend was not observed for the cis ions. It must, however, be said that the ammine-complexes always have a stronger affinity for a cation exchanger than the corresponding ethylenediamine-complexes; this also be due to the differences of size between ammonia and ethylenediamine molecules.

In the present work, we wanted to study many complexes of the diacido-type, but we were limited by the solubility of the complexes. However, through all the experiments it is to be noted that this kind of technique is useful for distinguishing isomeric forms of complexes, apart from the practical separation of the isomers.

## Summary

Additional elution experiments for confirming the fact that the trans ions of the diacido-tetrammine-type complexes are always eluted faster than the corresponding cis ions have been performed by using several diacido-type complexes which are relatively unstable. By comparing the elution maxima for the whole complex ions which have been used to date, the relative adsorbabilities of the isomeric ions on a cation exchanger have been predicted as follows:

For the trans ions,

$$[Co\,en_2(NCS)_2]^+ < [Co\,en_2(NO_2)_2]^+ \simeq [Co\,en_2Br_2]^+ < [Co\,en_2Cl_2]^+ \simeq [Co\,en_2NO_2Cl]^+ < [Co(NH_3)_4(NO_2)_2]^+ < [Co\,en(NH_3)_2Cl_2]^+$$

For the cis ions,

$$[Co\,en_2Cl_2]^+ < [Co\,en_2(NCS)_2]^+ < [Co\,en(NH_3)_2Cl_2]^+ \simeq [Co\,en_2NO_2Cl]^+ < [Co\,en_2(NO_2)_2]^+ < [Co(NH_3)_4(NO_2)_2]^+$$

A part of the present work was supported by a grant-in-aid from the Ministry of Education.

*Department of Chemistry*
*Faculty of Science*
*Kanazawa University*
*Kanazawa*

# *The Beckmann Rearrangement of 1, 2-Cyclohexane-dione Dioxime in Liquid Sulfur Dioxide*[1]

By Niichiro TOKURA, Ritsuro TADA and Kunio YOKOYAMA

(Received March 8, 1961)

The Beckmann rearrangement of 1, 2-diketone dioxime has scarcely been reported on except in the case of benzil dioximes[2]. In the present article the authors wish to reports on the Beckmann rearrangement of 1, 2-cyclohexanedione dioxime in liquid sulfur dioxide, which resulted in a variety of interesting products.

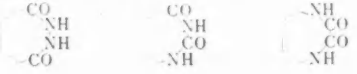
Several examples of the Beckmann rearrangement, in which the directions of the course of the rearrangement were affected by difference in the reagents applied or conditions used have been published. In a report of Brown, van Gulic and Schmid[3], for instance, the migratory aptitude of pivalophenone oxime was found to be largely dependent upon the nature of the reagent applied, the oxime being subjected to geometrical isomerization before rearrangement[3]. The present authors have also observed that the Beckmann rearrangement of 1, 6-cyclodecanedione dioxime yielded different products accoding to the different reagents used in the rearrangement. Such complicated results have also been reported by McLaren and Schacht[5], and Yukawa and his associates[6]. However, one of the anomalies during the rearrangement, the occurrence of the syn-anti isomerization of the oximes before the rearrangement, can be largely reduced as was reported in a recent article[7] if the reaction is conducted in liquid sulfur dioxide.

In a preceding paper[8], the present authors reported on their unsuccessful attempt at the Beckmann rearrangement of 1, 2-cyclohexanedione dioxime (I) with thionyl chloride in liquid sulfur dioxide. They obtained only a dehydrated product, cyclohexano[c]-1, 2, 5-oxadiazole (II) in a yield of 70 per cent.

I II

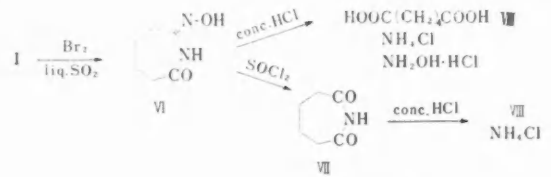
Although the reaction with thionyl chloride was unfruitful, however, the bromine in liquid sulfur dioxide and the sulfur trioxide in sulfur dioxide afforded the rearranged products with which the present paper is concerned.

As 1, 2-cyclohexanedione dioxime (I) has not been found to have geometrical isomers and as the various reagent examined in this material have given no symptom of the presence of geometrical isomers, the problem of the possible isomer was excluded in this experiment. In view of the authors' experience with the Beckmann rearrangement, it is interesting to examine the formation of the three possible cyclic acidamide III, IV, V or the mixture of these compounds in the reaction products. But the transformation to any of these three has not been observed.




III IV V

Bromine in liquid sulfur dioxide yielded a half-rearranged product as follows:




1) The Beckmann Rearrangement in Liquid Sulfur Dioxide. Part VIII.
2) J. Meisenheimer and W. Lamparter, *Ber.*, **57**, 276 (1924).
3) R. F. Brown, N. M. van Gulic and G. H. Schmid, *J. Am. Chem. Soc.*, **77**, 1094 (1955).
4) N. Tokura, R. Tada and K. Suzuki, This Bulletin, **32**, 654 (1958).
5) A. D. McLaren and R. E. Schacht, *J. Org. Chem.*, **14**, 254 (1949).
6) Y. Yukawa, "Jikken Kagaku Koza", Vol. 18, Maruzen, Tokyo (1958), p. 426.
7) R. Tada, Y. Masubuchi and N. Tokura, This Bulletin, **34**, 209 (1961).
8) Part VII of this series, This Bulletin, **34**, 270 (1961).

The product was contaminated with a large amount of brown resinous matter from which white crystalline substances VI were isolated by acetone extraction in a yield of 32 per cent. A very small amount of II was also found in the mixture. The substance VI, m. p. 155°C, was soluble in water, acid, base, ethyl alcohol and acetone respectively but was insoluble in ether, benzene and chloroform. When VI was subjected to hydrolysis with concentrated hydrochloric acid, adipic acid, ammonium chloride[9] and hydroxylamine hydrochloride[10] were identified in the reaction mixture; no hydrazine salt was found in the mixture[11], however, the infrared spectrum of VI also proved the presence of OH and NH (2900~3200 $cm^{-1}$, strong and broad) and carbonyl (1620~1600 $cm^{-1}$, strong) groups. Moreover, the NMR spectrum of VI in dimethylsulfoxide confirmed the presence of =NOH and =NH, as in Fig. 1[12]. The peak of the oximine group was consistent with that of cyclohexanoxime, and the very low and broader absorbancy in the higher field corresponded to that of the imino group.

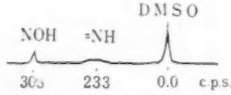



Fig. 1. NMR spectrum of VI in DMSO. c. p. s. was taken with that of DMSO as standard.

Thus the structure of VI was established as 1-aza-7-oximinocyclohepta-2-one. In order to effect the rearrangement of the remaining oximino group of VI, VI was further subjected to a reaction with thionyl chloride in ether. The resultant product seemed likely to be adipic imide (VII)[13], the oximino group being eliminated from VI without accepting further rearrangement. The hydrolysis of VII with concentrated hydrochloric acid afforded adipic acid (VIII) and ammonium chloride. The infrared spectrum of VII was agreeable with that of cyclic imide as reported by Vegstky et al.[14]

The attempted rearrangement with sulfur trioxide in liquid sulfur dioxide was accompanied by a large resinous matter. By extracting the viscous reaction mixture with ether, an orange oil (IX) was obtained. The oil boiled at 181~183°C/17 mmHg, and its yield was 23 per cent.

$$\mathrm{I} \xrightarrow[\text{liq. } SO_2]{SO} \underset{NH_2OH}{NC-(CH_2)_4-COOH} \xrightarrow{\text{conc.HCl}} \mathrm{VIII}$$

IX

The compound IX was identified as $\delta$-cyanovaleric acid from the elemental analysis, the infrared spectrum, the hydrolysis to adipic acid, the esterification and the saponification value of the ester. The present authors also found hydroxylamine in the residue of the reaction mixture by the diacetyl monoxime method[10]. Thus, the cleavage of I to IX seems likely to pass through an intermediate, 1,2-cyclohexanedione 2-monoxime (X), which might be derived through partial hydrolysis of an oximino group of I, the so-called Beckmann rearrangement of the second order being followed. An alternative explanation is also conceivable and will be discussed later.

## Experimental

**Materials.**—Commercial sulfur dioxide was dried with concentrated sulfuric acid[15] and distilled.

Bromine was dehydrated with concentrated sulfuric acid and distilled. Sulfur trioxide of extra pure grade was used without further purification. 1,2-Cyclohexanedione dioxime (I) was synthesized[9] from 2-halo-cyclohexanone by reacting with hydroxylamine in yields of 10 to 34 per cent.

**Infrared Spectrum.**—A Perkin Elmer model 21 infrared spectrophotomer was used.

**NMR Spectrum.**—A Varian Associates' type V-4300 (40 mc.) nuclear magnetic resonance spectrometer was used.

**Reaction of Bromine on I.**—The dioxime(I) (14.2 g.) and bromine (35.2 g.) were reacted in 150 ml. of liquid sulfur dioxide at room temperature for one hour. When the reaction was over, the solution was poured into ice-water, the sulfur dioxide was evaporated and the residue was extracted with ether. From the ether extract, colorless crystals were obtained after the condensation of the solution. This substance was identified as cyclohexano-[c]-1,2,5-oxadiazole (II), which had already been produced and confirmed by the reaction of thionyl chloride on I in liquid sulfur dioxide[5], by its m. p. and mixed m. p. of 25.5~26.0°C: the yield was 0.6 g. (4%). The residual solution was neutralized with sodium carbonate and extracted with chloroform. Seven grams of resinous material was obtained from the solution, but the nature of this material was obscure.

The residual solution of the chloroform extraction was condensed in vacuo and triturated with acetone. On the evaporation of acetone, 4.6 g. (32%) of colorless crystals resulted. This crystal, VI, melting at 155°C (from water or ethyl alcohol), was soluble in water, acid, base, ethyl alcohol and acetone respectively but was insoluble in ether, benzene and

9) By Nessler reagent.
10) W. Hirscher and J. A. Verboeff, *Chem. Abstr.*, **17**, 2845 (1923).
11) L. Szebelledy and V. Madis, ibid., **31**, 6128 (1937).
12) The NMR spectrum was taken by the courtesy of Prof. T. Isobe.
13) E. N. Zilbermann, *Chem. Abstr.*, **50**, 8458 (1956); H. K. Hall, Jr. and A. K. Schneider, *J. Am. Chem. Soc.*, **80**, 6411 (1958).
14) A. Vegstky, K. Harada and S. W. Fox, *J. Am. Chem. Soc.*, **80**, 336 (1958).
15) D. Murakami and N. Tokura, This Bulletin, **31**, 431 (1958).

chloroform. The elemental analysis showed no difference to the starting oxime I, suggesting that a rearrangement was undertaken in this reaction.

Found: C, 51.21; H, 6.85; N, 19.68. Calcd. for $C_6H_{10}O_2N_2$: C, 50.69; H, 7.07; N, 19.71%. IR $\nu_{max}^{KBr}$ 2900~3200 (strong and broad, -OH and =NH); 1660 (strong and broad, =CO) and 1620 weak, -C=N) $cm^{-1}$, respectively.

**Hydrolysis of VI.**—VI (2.0 g.) was refluxed for 2 hr. in concentrated hydrochloric acid. After the reaction, the colorless needles (III) so produced were filtered and recrystallized from ethyl alcohol, 1.1 g., m. p. 151~152°C. The mixed melting point with adipic acid showed no depression.

Found: C, 49.46; H, 6.94. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.90%.

The filtrate was evaporated to dryness. This residue contained ammonium chloride (Nessler test). Also hydroxylamine hydrochloride was identified[10]. No hydrazine salt was found in the residual mixture[11].

**Reaction of IV with Thionyl Chloride.**—VI (0.5 g.) was refluxed in ether (20 ml.) with thionyl chloride (0.5 g.) for fifteen minutes. The reaction mixture was poured into ice-water, and white powder (0.2 g.), m. p. 166.5°C., was yielded by the ethereal solution. This compound VII was assumed to be adipic acid imide from the elemental analysis, the infrared spectrum and the hydrolysis with concentrated hydrochloric acid to adipic acid (VIII), the melting point and the mixed melting point being 152°C.

Found: N, 1030. Calcd. for $C_6H_9O_2N$: N, 11.02%. IR $\nu_{max}^{KBr}$ 3200 and 3350, (strong, =NH), 1700 (=CO) and 2950 (=$CH_2$) $cm^{-1}$, respectively. From the reaction mixture of the hydrolysis, after the filtration of the afforded adipic acid, neither hydrazine nor hydroxylamine salt was identified by the procedure described above.

**Reaction of I with Sulfur Trioxide.**—I (7.1 g.) and sulfur trioxide (10.0 g.) were reacted in 100 ml. of sulfur dioxide for one hour at room temperature. The reaction mixture was poured into ice-water, after which the sulfur dioxide was allowed to evaporate and was then extracted with ether. The ethereal solution was washed with water, dried and evaporated. An orange-colored liquid (IX), boiling at 181~183°C/17 mmHg, $n_D^{17}$=1.4452, 1.6 g. (23%), was obtained and identified as $\delta$-cyano-valeric acid, (literature[16], b. p. 158~160°C/5 mmHg, $n_D^{20}$=1.4481).

The residual solution after the extraction contained a large amount of resinous matter which could not be further examined.

Found: N, 10.53. Calcd. for $C_6H_9O_2N$: N, 11.02%. IR $\nu_{max}^{liq.}$, 3000~3300 (strong and broad, -OH), 2260 (medium, -CN) and 1700 (strong, =CO) $cm^{-1}$, respectively.

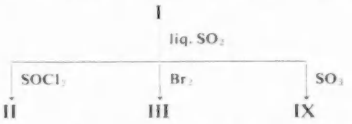
**Hydrolysis of IX.**—IX (0.3 g.) was reacted with 3 ml. of concentrated hydrochloric acid by refluxing. On cooling of the reaction mixture, colorless needles were obtained in the mixture, which on admixture with adipic acid (VIII) showed no depression of the m. p. of 151~152°C.

**Esterification of IX.**—IX (2.0 g.) and two drops of concentrated sulfuric acid in 4 ml. of absolute ethyl alcohol were refluxed for 24 hr. The mixture was then mixed with water, and the separated oil was dried and distilled. An oil of b. p. 252~256°C 760 mmHg, (reportedly[16] 145~150°C/24 mmHg), was obtained. This oil was consistent with ethyl $\delta$-cyano-valerate.

Found: C, 60.83; H, 8.37; N, 8.44. Calcd. for $C_6H_{11}O_2N$: C, 61.91; H, 8.44; N, 9.03%. Sapon. value, Found, 706.5, Calcd., 722.5.

## Discussion

When I was reacted with three different reagents, thionyl chloride, bromine and sulfur trioxide respectively, in liquid sulfur dioxide, for one hour at room temperature, three different products were obtained, viz., cyclohexano[c]-1, 2, 5-oxadiazole (II), 1-aza-7-oximino-cycloheptа-2-one (VI) and $\delta$-cyano-valeric acid (IX) respectively, among which the first has been presented in a preceding paper[5].




If the reactions were performed without sulfur dioxide, no such simple product was obtained. Thus, thionyl chloride yielded much resinous matter, and II was obtained in a yield of zero to ten per cent. Bromine afforded only nitrosobromo compound, the presence of which was recognized by the blue color formation. Sulfur trioxide also produced a large amount of resin. This means that the reaction in liquid sulfur dioxide was greatly favored by the assistance of the solvation of this solvent, which enabled the reaction to be carried out at a lower temperature and to avoid various side reactions.

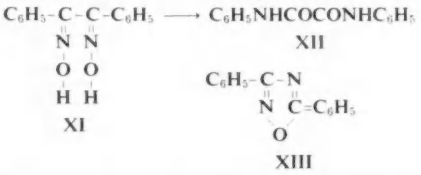
The results obtained above may be useful to enhance our understanding of the mechanism of the Beckmann rearrangement in liquid sulfur dioxide. Not only were the three products different, but the features of the respective processes were entirely different.

They were a dehydrative condensation, a Beckmann rearrangement of one of the two oximino groups, and a ring cleavage reaction respectively. The Beckmann rearrangement of 1, 2-diphenyl-1, 2-dione dioxime (benzil dioxime) which reportedly consisted of three geometrical isomers, has already been reported[17]. According to Meisenheimer and Lamparten[2], the $\beta$-isomer of XI afforded oxanilide XII, both of the two oximino groups rearranging, whereas $\alpha$- and $\gamma$-isomers yielded

16) R. H. Wiley and H. S. Morgan, Jr., *J. Org. Chem.*, **15**, 800 (1950); W. Reppe, *Ann.*, **596**, 127 (1955).

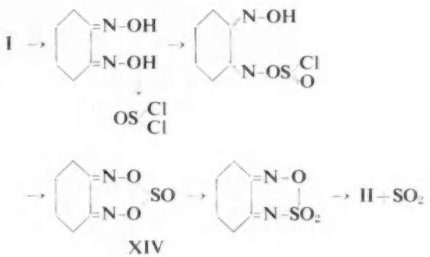
17) a) K. Awers and V. Meyer. *Ber.*, **21**, 810 (1888). b) E. Beckmann and A. Koster, *Ann.*, **274**, 18 (1893). c) E. Gunther, *Ber.*, **21**, 516 (1888); *Ann.*, **257**, 276 (1889).

3, 5-diphenyl-1, 2, 4-oxadiazole (XIII), a product of one oximino group rearrangement followed by dehydration. The reagent used were thionyl chloride and phosphorus compounds.



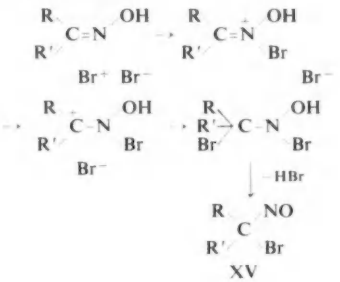
That a simple dehydration occurred by thionyl chloride from I to II indicates that the rate of the Beckmann rearrangement of I with thionyl chloride was much less than the rate of condensation with the same reagent in liquid sulfur dioxide. In such a cyclic dioxime as I, the steric impedence by the ring enlargement, if it arose, would be considerable. On the other hand, in the case of XI, no steric hindrance was anticipated, and the formation of azilinium cation favorable for the Beckmann rearrangement may be greatly assisted by the participation of the phenyl group.

The predominance of the condensation reaction between the two competitive reaction is a result of the nature of the reagent (thionyl chloride). A=N·O·SOCl group formed from a reaction between thionyl choride and a oximino group will easily produce a sulfite linkage XIV by reacting with another oximino group, for these two groups are occupying positions very close to each other. Consecutively, the formation of a sultone via the Bissinger rearrangement[18] and the conversion of the sulfite to II by elimination of the sulfur dioxide molecule would be undertaken. Very recently, Gillis[19]

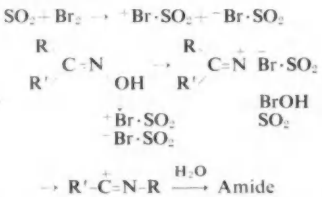


has reported the formation of tetrahydrofuran from 1, 4-tetramethylene glycol with thionyl chloride via the sulfite. The derivation of II from I closely resembles this furan formation.

Here, the behavior of bromine in liquid sulfur dioxide is very interesting. When the reagent is bromine only, without sulfur dioxide, the bromine cation will attack the nitrogen atom of the oxime:

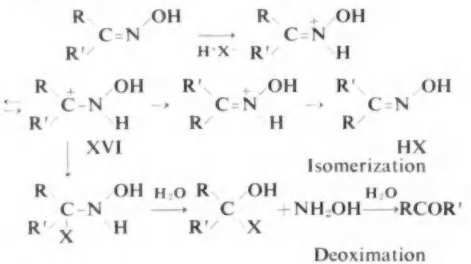


Producing a nitroso bromo compound XV which is characteristically blue in color. However, the bromine in sulfur dioxide[20] may attack the oxygen atom of the oxime, since the voluminous $SO_2$-solvated bromo-cation is liable to prefer the oxygen atom to the nitrogen atom; this would be followed by the rearrangement:



The reason why only one of the two oximino groups will accept the rearrangement is perhaps due to the steric hindrance.

Generally speaking, the attack of hydrogen acid causes some complex results in the attempted Beckmann rearrangement. The side reactions are the isomerization[5,21] of the oxime and the deoximation of the oxime (ketone formation)[21]. The origin of both arises from the same source, the formation of a carbonium ion, XVI:



18) W. Bissinger, F. E. King and C. W. Hamilton, *J. Am. Chem. Soc.*, **70**, 3940 (1948).
19) R. G. Gillis, *J. Org. Chem.*, **25**, 651 (1960).
20) N. Tokura, R. Asami and R. Tada, *J. Am. Chem. Soc.*, **79**, 3135 (1957).
21) R. Tada, Y. Masubuchi and N. Tokura, This Bulletin, **34**, 270 (1961).

There are many examples of carbonium ion formation from oxime with hydrogen acid, such as hydrochloric acid, sulfuric acid and hydrogen cyanide[21,22]. Such a carbonium ion (XVI) cannot undertake the Beckmann rearrangement. To carry out the rearrangement, an ion-pair formation

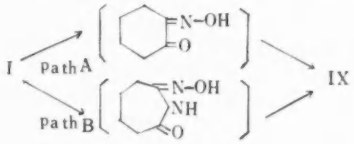
$$=N\text{-}O\text{-} \longrightarrow =\overset{+}{N}\ \overset{-}{O}\text{-}$$

between the two atoms is necessary[23].

The cleavage of I to IX is presumed to pass through an intermediate, 1, 2-cyclohexanedione monoxime (X), which may result from a partial deoximation of I, the so-called Beckmann rearrangement of the second order being followed (path A). A small amount of water remaining in the solvent (sulfur dioxide) may be responsible for the deoximation by serving as a source of the proton,

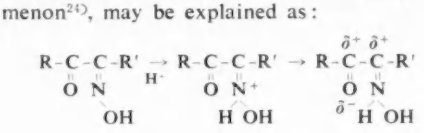
$$SO_3 + H_2O \rightarrow H^+ + SO_4H^-$$

An alternate path B might be considered.



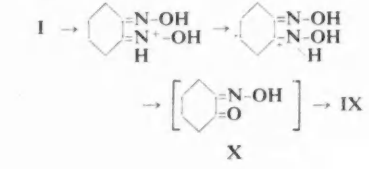

However, path B must be ruled out because this route cannot explain the presence of hydroxylamine in the reaction mixture.

The dioxime I has two oximino group sterically interferring with each other, and the elimination of one of the oximes would be a natural consequence. It is a plausible conclusion that I was cleaved to IX, via the stage of cyclohexanedione monoxime (X), the deoximation being effected by sulfuric acid mentioned above. As the result of the material balance of the IX formation, a large amount of resinous matter was recognized. Such a resinification by a dehydration reaction would supply enough water to make the proton source available for the deoximation. The Beckmann rearrangement of the second order, a well-discussed phenomenon[24], may be explained as:



$$\rightarrow R\cdot\overset{+}{C}O + R'CN \xrightarrow{OH^-} RCOOH + R'CN$$

Summarizing the above discussion, the formation of $\delta$-cyanovaleric acid (XI) may be visualized as:




X

## Summary

Three different reagents, thionyl chloride, bromine and sulfur trioxide in liquid sulfur dioxide were reacted on 1, 2-cyclohexanedione dioxime to yield cyclohexano[c]-1, 2, 5-oxadiazole, 1-aza-7-oximinocyclohepta-2-one and $\delta$-cyanovaleric acid respectively. Only the bromine in liquid sulfur dioxdie effected the Beckmann rearrangement. Thionyl chloride caused a dehydrative condensation, as has been reported previously. Sulfur trioxide yielded a product resulting from a deoximative cleavage. The reasons for the different processes and the different products have been discussed.

The authors are grateful to Befu Chemical Industries Inc., for the donation of liquid sulfur dioxide.

*The Chemical Research Institute of Non-Aqueous Solutions*
*Tohoku University*
*Katahira-cho, Sendai*

22) O. L. Brady and E. P. Dunn, *J. Chem. Soc.*, **109**, 656 (1916); G. Munch, *Ber.*, **29**, 62 (1896).
23) M. Kuhara, Y. Toda, *Memoirs Col. Kyoto Univ.*, **2**, 387 (1910).
24) D. Murakami and N. Tokura, This Bulletin, **31**, 1044 (1958); R. T. Conley and F. A. Mikulski, *J. Org. Chem.*, **24**, 97 (1959); A. F. Ferris, ibid., **24**, 580 (1959).

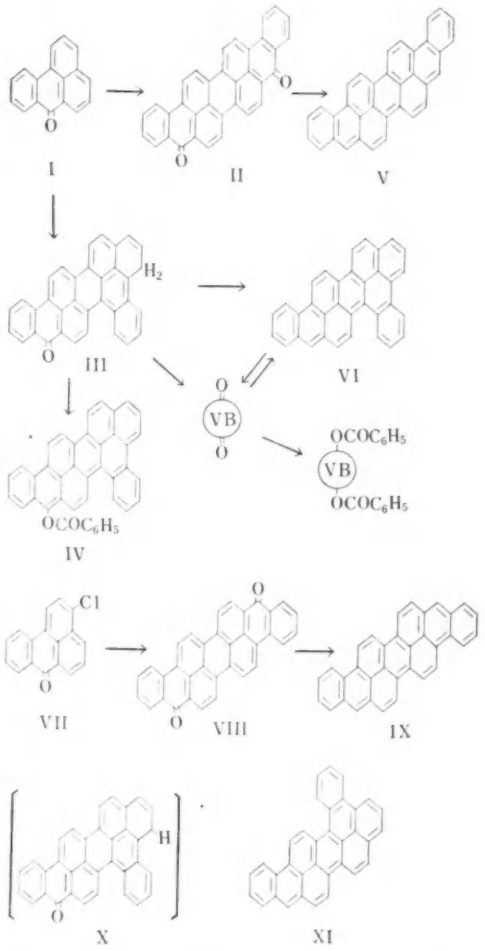
# *Studies of Violanthrone B. I. Reduction and Oxidation of Violanthrone B*[1]

By Junji Aoki

(Received March 18, 1961)

When benzanthrone (I) is fused with potassium hydroxide in the presence of phenol or sodium acetate, by its own condensation, violanthrone (II) is obtained; this substance is very useful as a vat dye. On the other hand, as a by-product, a black violet compound which is worthless as vat dye is obtained; this compound is barely vattable at 65~70°C. This worthless compound was found by the study of Maki and denoted as violanthrone B[2]. Further, he suggested III as its formula with one carbonyl group. Although this assumption has been partially confirmed by studies on the condensations of benzanthrone derivatives by Maki and Nagai[3], there remain many doubtful points. Furthermore, recently it has been found by Akamatu and Maekawa[4] that this substance was paramagnetic and that it may be a new radical compound to be known as formula X. Their studies are quite interesting and valuable in the field of the chemistry of this polynuclear system.

From the result of elementary analysis and the preparation of the leucobenzoate (IV) which was obtained by the author by the addition of benzoyl chloride to the vat solution, it has been found, however, that this substance has only one carbonyl group. Following the reduction technique of Clar[5], in which violanthrone A[6] was reduced to violanthrene A (V) with zinc dust in the mixed flux of zinc chloride and sodium chloride, the author obtained the reduction product from violanthrone B. This compound resembles violanthrene A, which shows a strong yellow green fluorescence in organic solvent and is green when dissolved in concentrated sulfuric acid. It is, however, evident that this substance is apparently different from violanthrene A; the reduced compound is more soluble than violanthrene A in organic solvent and the melting point of the former is 344°C (corr.), while that of the later is higher than 360°C[5,7]. In addition, this compound is not identical with isoviolanthrene (IX)[5] either, the reduction product of isoviolanthrone (VIII) prepared by




1) Read befroe the 13th Annual Meeting of the Chemical Society of Japan, April, 1960.

2) T. Maki, *J. Chem. Soc. Ind., Japan* (*Kōgyō Kwagaka Zasshi*), **35**, 1441 (1932); *Chem. Abstr.*, **27**, 1629 (1933).

3) T. Maki, ibid., **38**, 1390 (1935); *Chem. Abstr.*, **30**, 2008 (1936); T. Maki and A. Kikuchi, ibid., **43**, 763 (1940); *Chem. Abstr.*, **35**, 1783 (1941); Y. Nagai et al., ibid., **47**, 529 (1944).

4) H. Akamatu and T. Maekawa, Presented at the 13th Annual Meeting of the Chemical Society of Japan, April, 1960.

5) E. Clar, *Ber.*, **72**, 1648 (1939).

6) "A" is used to distinguish it from the B-compound.

7) E. Clar, *Ber.*, **76**, 458 (1943).

the bimolecular self condensation of 3-chlorobenzanthrone (VII), because isoviolanthrene is yellow green rather than green when dissolved in concentrated sulfuric acid and melts at a temperature higher than 360°C[5,7]. From the results of his chemical analysis, the author has concluded that the reduction product is a new hydrocarbon having a "dibenzanthrene" type skeleton. We denote this hydrocarbon violanthrene B (VI).

When violanthrene A was oxidized with dilute sulfuric acid and potassium bichromate, the author obtained violanthrone A. In an effort to obtain violanthrone B, violanthrene B (VI) was oxidized, but violanthrone B (III) was not obtained. The oxidized product is readily vattable at 30°C and cotton is dyed in it a dark violet. The result of elementary analysis suggested that it may be a quinone of a dibenzanthrene type. This assumption was confirmed by the author, who synthesized its leucodibenzoate at m. p. 335~336°C (corr.).

However, he has found the more interesting fact that the quinone can also be prepared from violanthrone B (III) by a similar operation. Further, from this quinone violanthrene B (VI) was obtained again by zinc dust fusion.

In conclusion, it is reasonable to suppose that all derivatives from violanthrone B have the same polynuclear skeleton, but not those of violanthrene A and isoviolanthrene A.

On the other hand, it has been confirmed by the author that violanthrone B has only one carbonyl group, and further, it has been reported by Nagai et al. that the 6-position of benzanthrone contributes to the formation of the B-compound[1]. Consequently, the hypothetic skeleton (IV), submitted by Maki, coincides with the above facts, but the isomeric formula XI must also be re-considered for the same reason. A detailed discussion will be presented in a later report.

## Experimental

**Violanthrone A (II) and Violanthrone B (III).**—These substances were prepared by the operation stated in Maki's paper[2], but for the purpose of increasing the yield of B-compound, the condition of the alkali fusion was somewhat modified as below. Benzanthrone (I) (10.0 g.) was fused with 40 g. of 85% potassium hydroxide and 4.2 g. of phenol at 220°C for 30 min. (Ref. 2: 81% potassium hydroxide, 12.4 g. of phenol, 1 hr.).

Violanthrone A was obtained as one product, vattable at 55°C and insoluble in chlorobenzene. Yield, 2.5 g. of violet black powder. The concentrated sulfuric acid solution shows a pure violet color.

The other product, which was barely vattable and insoluble in glacial acetic acid, was violanthrone B. Yield, 5.4 g. of violet black powder. It is soluble in concentrated sulfuric acid as a blue color[8].

Found: C, 91.47; H, 4.35. Calcd. for $C_{34}H_{18}O$ (III): C, 92.28; H, 4.10%.

**Leucobenzoate of Violanthrone B (IV).**—Violanthrone B (III) (0.50 g.) was vatted by heating with 10 g. of sodium hydroxide, 10 g. of sodium hydrosulfite and 200 ml. of water at 70°C and 5 g. of benzoyl chloride was added. The mtxture was shaked without heating for 2 hr. After being allowed to stand overnight, the precipitate was collected and washed neutral. Yield, 0.50 g. of dark brown powder. The product was recrystallized from xylene-petroleum ether, giving red brown needles, m. p. 327~328°C (uncorr.), 340~341°C (corr.). The product is soluble in organic solvent with a strong yellow green fluorescence and in concentrated sulfuric acid solution shows at first a blue color and then a blue green.

Found: C, 89.92; H, 4.19. Calcd. for $C_{41}H_{22}O_2$ (IV): C, 90.09; H, 4.06%.

**Violanthrene B (VI).**—Two gram of violanthrone B (III) in the form of fine powder, was kept with 2.0 g. of zinc dust in the mixed flux of 10 g. of zinc chloride and 2.0 g. of sodium chloride at 260°C for 20 min. Then the mixture was treated with 300 ml. of water and the insoluble material was filtered off. To remove the excess of zinc dust, it was suspended in 100 ml. of water and 30 ml. of concentrated hydrochloric acid was added. After being kept overnight, the insoluble was collected and washed neutral. The crude reduction product (1.8 g.) was sublimated in a high vaccum ($10^{-3}$~$10^{-4}$ mmHg) and recrystallized from 100 parts of *o*-dichlorobenzene, giving orange red needles, m. p. 328°C (uncorr.), 341°C (corr.). This product is soluble in organic solvent with a strong yellow green fluorescence, and in the concentrated sulfuric acid solution shows at first blue and then green, after which it changes no more.

Found: C, 95.56; H, 4.32. Calcd. for $C_{34}H_{18}$ (VI): C, 95.75; H, 4.25%.

**Violanthrene A (V).**—Synthesis was carried out by a method similar to that used for VI[9]. The crude product (1.8 g.) obtained from 2.0 g. of violanthrone A (II), was sublimated in high vaccum and refluxed with 100 g. of *o*-dichlorobenzene for 30 min. The small amount of soluble impurities was removed by hot filtration. Yield, 0.6 g. of brown red crystalline powder, m. p. 476~478°C (uncorr.)[10]. This substance is only with difficulty soluble in organic solvent and in a concentrated sulfuric acid solution shows green color.

**Isoviolanthrene A (IX).**—Synthesis was carried out by a method similar to that used for V. Yield, 32% from isoviolanthrone (VIII). Dark red crystalline powder, m. p. 506~508°C (uncorr.)[11]. The product is only with difficulty soluble in organic solvent and appears as a yellow green coloration in concentrated sulfuric acid.

**Oxidation of Violanthrene B.**—To a solution of

8) The sample was purified by means of chromatography on anhydrous sodium carbonate from *o*-dichlorobenzene.
9) Cf. also Ref. 5
10) Ref. 7, m. p. 478°C.
11) Ref. 7, m. p. 510°C.

1.00 g. of violanthrene B (VI) in 30 ml. of concentrated sulfuric acid was added, with cooling, 30 ml. of water. After cooling till the room temperature, 1.0 g. of potassium bichromate, which had been dissolved in 20 ml. of water, was added. The mixture was stirred for 3 hr. on a boiling water bath and, after being diluted with 300 ml. of water, was filtered. The unchanged VI was separated as the insoluble part by treating it with a 2% alkaline hydrosulfite solution at 30°C, and 0.95 g. of the oxidation product was obtained from the violet filtrate by air oxidation. The crude product, finely powdered, was boiled with 300 g. of *o*-dichlorobenzene with reflux for 2 hr., and insoluble impurities was removed by hot filtration. The filtrate was evaporated to a volume of about 100 ml. for crystallization. The crystal (0.65 g.) formed was recrystallized from chlorobenzene, giving black violet needles, melting point higher than 360°C. The product shows pure blue when dissolved in concentrated sulfuric acid and reddish violet in a hot organic solvent, but it is readily vattable at 30°C while III is with difficulty vatted even at 60°C.

Found: C, 88.74; H, 3.83. Calcd. for $C_{34}H_{16}O_2$: C, 89.46; H, 3.53%.

*Leucodibenzoate.*—The oxidation product (0.50 g.) was vatted by heating with 8 g. of sodium hydroxide, 10 g. of sodium hydrosulfite and 200 ml. of water at 50°C and 5.0 g. of benzoyl chloride was added. The mixture was shaked without heating for 2 hr. and allowed to stand overnight. The precipitate was then collected and the unchanged substance was removed by treating with an alkaline hydrosulfite solution as the insoluble part. The crude product (0.45 g.) was recrystallized repeatedly from *o*-dichlorobenzene-petroleum ether, giving orange brown needles, m. p. 322~323°C (uncorr.), 335~336°C (corr.). This product is only with difficulty soluble in alcohol, when dissolved in benzene, xylene and *o*-dichlorobenzene gives a strong yellow green fluorescence, and in a concentrated sulfuric acid solution gives a bluish green coloration.

Found: C, 85.96; H, 3.93. Calcd. for $C_{48}H_{26}O_4$: C, 86.47; H, 3.93%.

**Oxidation of Violanthrone B.**—By an operation similar to that used for VI, 2.00 g. of violanthrone B (III) was oxidized with 2.0 g. of potassium bichromate and diluted sulfuric acid, and 1.65 g. of crude product was obtained from an alkaline hydrosulfite vat as the soluble part (the insoluble, 0.30 g.). It was boiled with 300 g. of *o*-dichlorobenzene, and 1.00 g. of violet black needles of a melting point higher than 360°C were obtained from the filtrate after hot filtration. The product was easily vattable, was soluble in concentrated sulfuric acid, appearing as a pure blue color, and its absorption spectrum and leucobenzoate are identical with those of the oxidation product of violanthrene B.

*Reduction.*—By zinc dust fusion 0.20 g. of the above mentioned quinone was reduced. The crude product was purified by sublimation in high vacuum and recrystallization from *o*-dichlorobenzene. Yield, 0.06 g. of orange red needles, m. p. 326~328°C (uncorr.). This product was identical with violanthrene B (VI).

**Oxidation of Violanthrene A.**—By an operation similar to that used for VI, 1.00 g. of violanthrene A was oxidized with 1.0 g. of potassium bichromate and diluted sulfuric acid. The crude product was treated with 3% alkaline hydrosulfite solution at 60°C, and the unchanged substance was removed as the insoluble. From the red violet filtrate, 0.85 g. of the oxidation product was obtained. It was boiled with 100 g. of chlorobenzene for 1 hr., filtered and dried. Yield, 0.80 g. of violet black powder, melting point higher than 360°C. The product was soluble in concentrated sulfuric acid, giving a pure violet color, and, further, any other properties were also identical with those of violanthrone A (II) (Found: C, 89.11; H, 4.03%).

The author wishes to express his thanks to Professor Hideo Akamatu, Professor Hiroo Inokuchi and Professor Yoshio Nagai for their kind advice. He is also indebted to Mr. Shozo Masuda for carring out the analyses.

*Department of Chemistry*
*Facutly of Science*
*Toho University*
*Narashino, Chiba*

# *Studies of Violanthrone B. II. Reduction of Isoviolanthrone B*

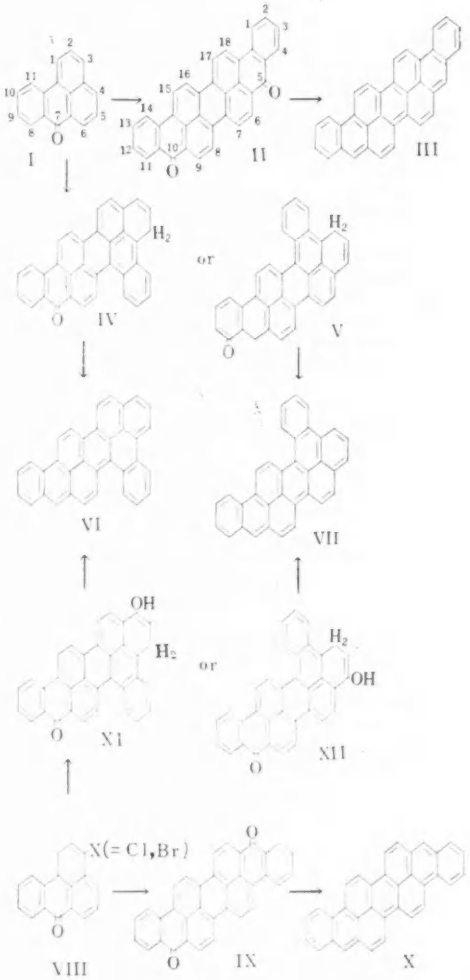
By Junji AOKI

(Received March 18, 1961)

As described in a previous paper[1], the reduction of violanthone B resulted in obtaining the new condensed aromatic hydrocarbon, violanthrene B. Generally, when the method of alkali fussion on benzanthrone (I) derivatives (except 3-position) is applied for the purpose of obtaining the vat dyes of the violanthron (II) series, the B-compound is by-produced with violanthrone derivatives. For example, 4, 11- and 1, 14-dimethoxyviolanthrone were prepared from 8- and 11-methoxybenzanthrone respectivery by alkali fusion, and B-compounds were also obtained[2]. Violanthrone B and these B-componds resemble each other in their vattability and in their coloration with concentrated sulfuric acid. It is, therefore, suggested that the B-compounds by-produced with A-compounds of the violanthrone A type may be derivatives of violanthrone B.

Further, Nagai and Masuda have reported that the 6-position of benzanthrone contributes to the formation of B-compound because the reaction of the alkali fusion of 6-phenylbenzanthrone produces A-compound, but not B-compound[3]. According to these facts, the formula VI or VII can be applied to the skeleton of B-compound, which has only one carbonyl group[4].

On the other hand, there is another type of B-compound, that by-produced with isoviolanthrone (IX) from 3-halogenobenzanthrone (VIII) by heating with alcoholic potassium hydroxide. This B-compound, which is as barely vattable as violanthrone B, has been denoted as isoviolanthrone B by Maki and Nagai[5], and they have suggested as the formula XI, in which the halogen atom was converted into the hydroxl group. In addition, Nagai et al. have reported that the reaction of the alcoholic alkali of 3-chloro-6-phenylbenzanthrone produces A-compound of the isoviolanthrone type, but not B-compound[3].




Therefore, although the formula (XI) appears feasible the isomeric formula (XII) may be also considered, as has been mentioned for violanthrone B[6].

The author has tried to reduce isoviolanthrone B to hydrocarbon by the method of

1) J. Aoki, This Bulletin, **34**, 1817 (1961).

2) T. Maki, *J. Chem. Soc. Ind., Japan*, **38**, 1390 (1935); *Chem. Abstr.*, **30**, 2008 (1936); T. Maki and A. Kikuchi, ibid., **43**, 763 (1940); *Chem. Abstr.*, **35**, 1783 (1941).

3) Y. Nagai and M. Masuda, *J. Chem. Soc. Ind., Japan*, **47**, 529 (1944).

4) Consequently, violanthrone B may be considered as having the formula IV or V; T. Maki has suggested IV as the formula.

5) T. Maki and Y. Nagai, *J. Chem. Soc. Ind. Japan*, **37**, 493 (1934); *Chem. Abstr.*, **28**, 5435 (1934).

6) These compounds may be considered free radical because of their paramagnetism; therefore, instead of formulas IV, V, XI and XII, those which take off one hydrogen atom should be preferred. See also Ref. 1.

TABLE I. PROPERTIES OF "DIBENZANTHRENES"

| | Violanthrene B | | Isoviolanthrene B | | Violanthrene A | | Isoviolanthrene A |
|---|---|---|---|---|---|---|---|
| Appearance | Orang red | | Deep red | | Red | | Dark red |
| M. p., °C | 344 | | 400~402 | | 478[7] | | 510[7] |
| Color in $H_2SO_4$ | Green | | Yellow green | | Green | | Yellow green |
| Solubility | | >[8] | | > | | > | |
| Alcohol | Insol. | | Insol. | | Insol. | | Insol. |
| Benzene | Hardly sol. | | Hardly sol. | | Hardly sol. | | Hardly sol. |
| *o*-Dichloro-benzene | Sol. in hot | | Sol. in hot | | Hardly sol. | | Hardly sol. |

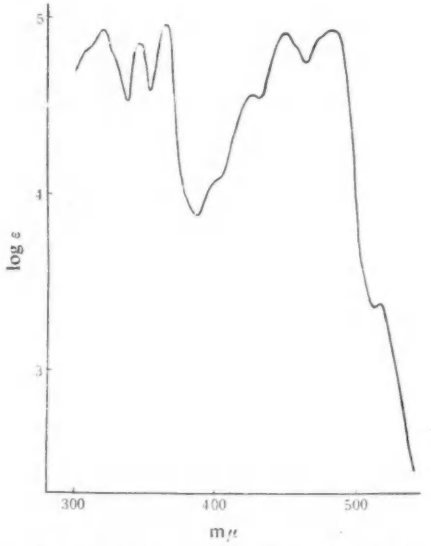



Fig. 1. Absorption spectrum of Violanthrene B (in benzene).

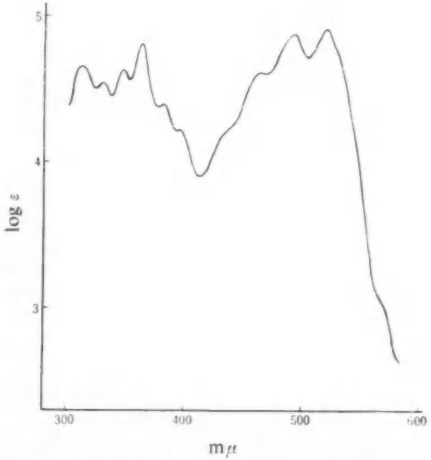



Fig. 2. Absorption spectrum of isoviolanthrene B (in benzene).

zinc dust fusion in order to find the structural formula of this compound. The hydrocarbon obtained from the above method recrystallized from *o*-dichlorobenzene in deep red needles. The meting point of this compound was 400~402°C (uncorr.), and its absorption spectrum was different from that of violanthrene B, as is shown in Figs. 1 and 2. In addition, the properties of this new hydrocarbon, which is called by the author isoviolanthrene B, are quite different from those of violanthrene B, violanthrene A (III) and also isoviolanthrene A (X), as is shown in Table I.

From these facts, we can draw the following conclusions: there are only two types of B-compound, with skeletons assumed to be the fosmulas VI and VII; one of them is violanthrene B and the other is isoviolanthrene B.

## Experimental

**Isoviolanthrone A (IX) and Isoviolanthrone B.**—A mixture of 40 g. of potassium hydroxide, 25 g. of phenol, 15 g. of ethanol and 10.0 g. of 3-chlorobenzanthrone was refluxed with stirring for 2 hr. Then the mixture was treated by the method described in Ref. 5. The yield of isoviolanthrone A was 3.2 g., and this substance is soluble in concentrated sulfuric acid, giving a blue green color. Isoviolanthrone B was obtained as the product, barely vattable and insoluble in glacial acetic acid. In the concentrated sulfuric acid solution it shows as a dark violet color. Yield, 3.0 g. of violet black powder. This sample was once more treated with an alkaline hydrosulfite solution, dissolved in hot chlorobenzene and, after hot filtration, deposited by concentrating the filtrate.

Found: C, 88.80; H, 3.58. Calcd. for $C_{34}H_{12}O_2$ (XI or XII): C, 89.06; H, 3.95%.

**Isoviolanthrene B.**—A fine powder of 1.00 g. of isoviolanthrone B was kept with 1.0 g. of zinc dust in the mixed flux of 5 g. of zinc chloride and 1 g. of sodium chloride at 260~280°C for 30 min. Then the mixture was treated with 300 ml. of water and the insoluble part filtered off. To remove the excess of zinc dust, it was suspended with 100 ml. of water, and 30 ml. of concentrated hydrochloric acid was added. After being kept overnight, the insoluble part was collected and washed neutral. The crude

7) E. Clar, *Ber.*, **76**, 456 (1943).
8) This symbol defined a solubilization power.

reduction product (0.80 g.) was sublimated in a high vacuum ($10^{-3}$~$10^{-4}$ mmHg), and recrystallized from *o*-dichlorobenzene, giving deep red fine needles, m. p. 400~402°C (uncorr.). This product is soluble in organic solvent, giving off a strong fluorescence, and in a concentrated sulfuric acid solution shows at first as green and then as a yellow green, after which it changed no more.

Found: C, 95.56; H, 4.34. Calcd. for $C_{34}H_{18}$ (VI or VII): C, 95.75; H, 4.25%.

The author wishes to express his thanks to Professor Hideo Akamatu, Professor Hiroo Inokuchi and Professor Yoshio Nagai for their kind advice. He is also indebted to Mr. Shozo Masuda for carrying out the analyses.

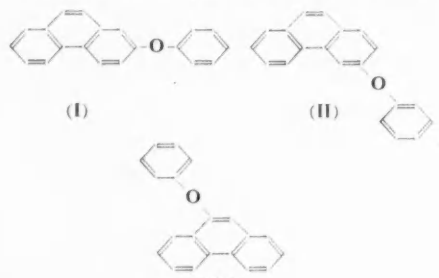
*Department of Chemistry*
*Faculty of Science*
*Toho University*
*Narashino, Chiba*

# *Synthesis of Phenanthryl Phenyl Ethers*

By Hajime SUZUMURA

(Received March 31, 1961)

Searching for aromatic ethers which have high boiling points and thermal stability, derivatives of phenanthrene, 2- and 3-phenanthrylphenyl ethers (Formulas I and II respectively) were synthesized and their physical properties examined. Of the phenanthrylphenyl ethers, only a 9-phenyl isomer (Formule III) has hitherto been reported on the literature[1].



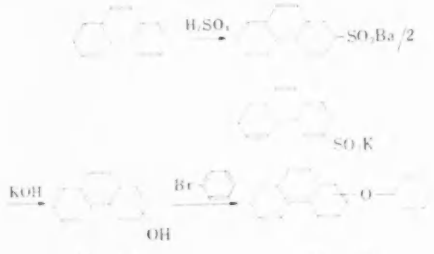
(I) (II)



(III)

The author newly synthesized 2- and 3-phenyl ethers by the scheme shown below.

TABLE I




(2-, 3-) (2-, 3-)

1) R. L. Huang, *J. Chem. Soc.*, **1955**, 3295.

Purified phenanthrene was sulfonated[2], and a mixture of monosulfonates was fused with potassium hydroxide[3], yielding phenanthrols which were then condensed with bromobenzene to give the ethers. The properties of purified specimens are shown in Table II.

TABLE II. PHENANTHRYLPHENYL ETHERS

| Properties | Isomer 2- | Isomer 3- | Calcd. |
|---|---|---|---|
| Appearence | White needles | White needles | — |
| B. p., °C | 225(1mmHg) | 220 (1 mmHg) | — |
| M. p., °C | 121~122 | 86~87 | — |
| Elementary analysis | | | |
| C, % | 88.69 | 89.16 | 88.86 |
| H, % | 5.00 | 5.39 | 5.22 |
| Trinitrobenzene complex | | | |
| M. p., °C | 133~134 | 111~112 | — |
| Appearence | Pale yellow needles | Pale yellow leaflets | — |
| N, % | 8.91 | 8.96 | 8.70 |

## Experimental

**Materials.** — *Phenanthrene.* — A sample supplied by Yawata Chemical Industry Co. was purified by fusion with potassium hydroxide, followed by vacuum distillation, recrystallization from ethanol and treatment with chromium trioxide; m. p. 97~98.5°C, reported 98.7~99.5°C[4].

*Bromobenzene.* — A commercial reagent was redistilled; $n_D^{26.5}$ 1.5598, reported $n_D^{20}$ 1.5602[5].

2) "Org. Synth.", Col. Vol. II (1955), p. 482.
3) Fieser, *J. Am. Chem. Soc.*, **51**, 2466 (1929).
4) J. Heilbron, "Dictionary of Org. Compds.", Vol. IV, Oxford University Press, New York (1953), p. 84.
5) Merck Index, 7th Edition, Merck & Co. Inc., Rahway, N. J. (1960), p. 168.

*Copper Powder.*—This was precipitated from an aqueous solution of $CuSO_4 \cdot 5H_2O$ by the addition of zinc granules and was washed with water, with dilute hydrochloric acid, and finally with ethanol.

*Sulfuric Acid, Potassium Hydroxide.*—Commercial reagent.

**Synthesis of 2- and 3-Phenanthrol.** — Purified phenanthrene (50 g.)* was sulfonated by the method described in the literature[2]. From the reaction mixture, less soluble mono-sulfonic acids were separated as sodium salts, leaving disulfonates in the filtrate. By recrystallizing sodium mono-sulfonates from water, the relatively insoluble 2-isomer was first obtained, which was further purified as barium salt. From the filtrate, by concentration and the addition of potassium chloride, potassium 3-sulfonate was obtained. 2-Ba-sulfonate; 14.1 g., 16% (reported 17~21%). 3-K-sulfonate; 17.6 g., 21% (reported 24~26%). Then the sulfonates were fused with potassium hydroxide. To potassium hydroxide (about 3 parts) melted in a nickel crucible at 290~300°C, barium or potassium sulfonate (1 part) was added gradually over a period of 20 min. by stirring; the heating was continued for a further 5 min. at 320~330°C. The mixture was then allowed to cool and was dissolved in water. The addition of hydrochloric acid to this solution yielded a precipitate which was filtered off.

The precipitate was redissolved in an aqueous solution of potassium hydroxide and filtered off to remove insoluble matter. By the neutralization of the filtrate, crude phenanthrols were obtained which were filtered off and recrystallized from a mixture of ligroin and ethanol. The results of the potassium hydroxide fusion are shown in Table III.

TABLE III

| Phenanthrene sulfonate | Amount g. | Phenanthrol Amount g. | Phenanthrol M. p. °C | Reported m. p. °C |
|---|---|---|---|---|
| 2-Ba | 14 | 5.5 | 162.7~167.7<br>166~168 (purified) | 168 |
| 3-K | 17 | 10.3 | 112.6~118.5<br>116.8~118.9 (purified) | 118~119 |

**Synthesis of 2-Phenanthryl Phenyl Ether.** — A mixture of 2-phenanthrol, potassium hydroxide bromobenzene and copper powder in a flask fitted with an air condenser was placed in an oil bath and heated. The cooled mixture was first treated with a 10% aqueous solution of potassium hydroxide to dissolve unreacted phenanthrol and was then extracted repeatedly with benzene. The combined extracts were concentrated and distilled in vacuo. The distillation apparatus employed was designed for distilling solid samples and equipped with a fractionating column (10 mm. × 350 mm.) packed with stainless Dixon packing 2 mm. in diameter. The distillate, which was solid melting at about 110~116°C, was recrystallized 3 times from ethanol, yielding white needles. The experimental results of the condensation reaction are shown in Table IV.

* One tenth of the amount used in Ref. 2.

Found: C, 88.69; H, 5.00; mol. wt. (Rast), 273. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22%; mol. wt. 270.

*Infrared Absorption Spectrum.*—The spectrum of 2-phenanthryl phenyl ether in carbon bisulfide is shown in Fig. 1. The band appearing at 825 $cm^{-1}$

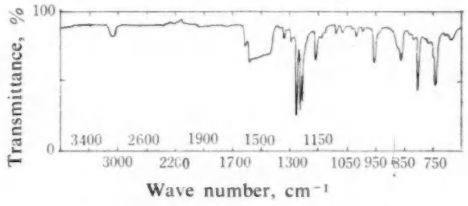



Fig. 1. 2-Phenanthryl phenyl ether.

corresponds to a 1,2,4-substitution in the benzene ring. This means a substitution in the 2- or 3-position of phenanthrene, which may be regarded as a substituted benzene. Similarly, because an absorption band at 807 $cm^{-1}$ which corresponds to a 1,2,3,4-substitution in benzene is absent, the 9- or 10-position of phenanthrene is not substituted. The absence of a strong absorption in the region of 752~753 $cm^{-1}$ shows that a 1,2,3-substitution in the benzene ring is not present; that is, there is no substitution in the 1- or 4-position of phenanthrene. The spectrum which shows characteristic absorptions of 2- or 3-substituted phenanthrene can be clearly distinguished from that of a 3-phenyl isomer, which will be described later. A band at 690 $cm^{-1}$ may be assigned to a phenoxy group. Phenoxynaphthalenes ($\alpha$, $\beta$), *p*-phenoxydiphenyl, and *p,p'*-diphenoxydiphenyl which the author prepared showed a medium absorption in the vicinity of this wave number.

*Ultraviolet Spectra.*—The spectra of the 2-phenyl as well as the 3-phenyl isomer are shown in Fig. 2.

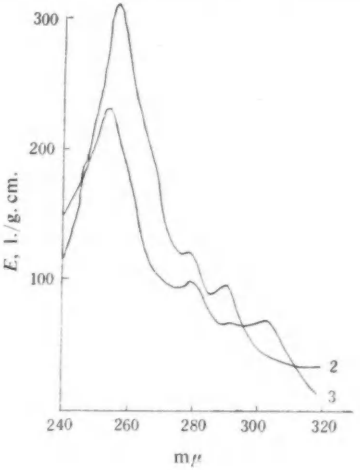



Fig. 2

2, 2-Phenyl isomer; 3, 3-Phenyl isomer

TABLE IV. 2-PHENANTHRYL PHENYL ETHER

| No. | 2-Phenanthrol[a] g. | Bromobenzene g. | KOH g. | Cu g. | Condition Temp. °C | Condition Time hr. | Distillate g. | Recrystallized Amount g. | Recrystallized M. p. °C | Recrystallized Yield[b] % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.2 | 3.1 | 1.3 | 0.2 | 150~200 | 2 1/3 | 3.1 | 1.6 | 120~121 | 27 |
| 2 | 1.1 | 2.0 | 0.35 | 0.05 | 170~185 | 3 5/6 | 0.89 | 0.45 | 120~121 | 29 |
| 3 | 4.2 | 5.9 | 1.3 | 0.2 | 140~200 | 5 | 4.5 | 2.50 | 121~122 | 43 |

a) M. p. of phenanthrol; Nos. 1 and 2, 162.7~167.7°C; No. 3, 166~168°C.
b) Mol. % based on 2-phenanthrol employed.

TABLE V. 3-PHENANTHRYL PHENYL ETHER

| No. | 3-Phenanthrol[a] g. | Bromobenzene g. | KOH g. | Cu g. | Condition Temp. °C | Condition Time hr. | Distillate g. | Recrystallized Amount g. | Recrystallized M. p. °C | Recrystallized Yield[b] % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5.5 | 4.0 | 1.7 | 0.20 | 150~200 | 5 1/2 | 5.3 | 2.35 | 85~86 | 31 |
| 2 | 3.1 | 5.4 | 1.0 | 0.13 | 160~170 | 4 1/2 | 1.99 | 1.32 | 86~87 | 31 |
| 3 | 4.2 | 5.9 | 1.3 | 0.20 | 140~200 | 5 | 4.8 | 2.95 | 86~87 | 50 |

a) M. p. of 3-phenanthrol; Nos. 1 and 2, 112.6~118.5°C; No. 3, 116.8~118.9°C.
b) Mol. % based on 3-phenanthrol employed.

The absorption maxima are different from those of 2- or 3-alkyl phenanthrene.

*Solubility*.—It is only with difficulty soluble in cold ethanol, readily soluble in benzene, and insoluble in water.

*Trinitrobenzene Complex*.—This was prepared from 2-phenanthryl phenyl ether (86 mg.) and 72 mg. of trinitrobenzene in ethanol. Three recrystallizations from ethanol yielded 45 mg. of short yellow needles, which melted at 133~134°C.

Found: N, 8.91, Calcd. for $C_{26}H_{17}O_7N_3$; N, 8.70%.

**Synthesis of 3-Phenanthryl Phenyl Ether.**—The 3-phenyl isomer was prepared and purified in the same manner as in the case of the 2-phenyl isomer. The experimental results are shown in Table V.

Recrystallization from ethanol gave white needles which melted at 86~87°C.

Found: C, 89.16; H, 5.39; mol. wt. (Rast), 273. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22%; mol. wt., 270.

*Infrared Spectrum*.—The spectrum in carbon disulfide is shown in Fig. 3.

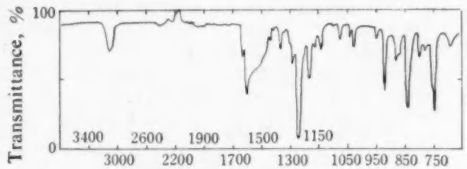



Fig. 3. 3-Phenanthryl phenyl ether.

A band at 690 $cm^{-1}$ corresponds to a phenoxyl group. Other absorption bands appearing in the finger print region are typical of 3-substituted phenanthrene, as a comparison with those of 3-ethylphenanthrene[6] shows:

| | Wave numbers, $cm^{-1}$ | | | | |
|---|---|---|---|---|---|
| 3-Phenanthryl phenyl ether | 880 | 865 | 840 | 798 | 747 |
| 3-Ethylphenanthrene | 881 | 864 | 839 | 800 | 746 |

*Ultraviolet Spectrum*.—The spectrum is shown in Fig. 2.

*Solubility*.—It is only with difficulty soluble in cold ethanol, moderately soluble in benzene, and insoluble in water.

*Trinitrobenzene Complex*.—This was prepared from ether (99 mg.) and trinitrobenzene (108 mg.) in ethanol. Three recrystallizations from ethanol yielded 73 mg. of a pale yellow adduct, m. p. 111~112°C.

Found: N, 8.96. Calcd. for $C_{26}H_{20}O_7N_3$, N, 8.70%.

The author is indebted to Professor Ryozo Goto of Kyoto University for his helpful discussions and for his criticisms of this work, and to Professor Sakujiro Kimura for his advice and encouragement.

*Tokyo Laboratory of Research Center*
*Yawata Chemical Industry Co.*
*Chuo-ku, Tokyo*

6) E. Ochiai, et al., *Pharm. Bull.*, **5**, 113 (1957).

# *Studies on Isoprenoide. XIII. Transformation of Pinene by the Action of Boron Trifluoride*

By Kimiko NAGAI

(Received March 25, 1961)

The transformation in the reaction of various reagents upon pinenes have been investigated[1-4] in detail, and the existence of camphene has been observed in the conversion products of pinene in almost all cases. The author has been engaged in a series of experiments on the reaction of boron trifluoride, an electrophilic agent, upon terpenes. It has been reported[5] that the reaction of boron trifluoride upon terpenes produces mainly polymerized products; my experiments seen to verify this.

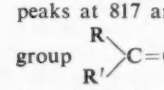
According to another paper[6] stating that isoborneol was produced by the reaction of glacial acetic acid upon camphene with a catalyst of boron trifluoride, the author has obtained bornyl acetate in a considerable yield in the reaction of glacial and anhydrous acetic acids upon $\alpha$-pinene with a catalyst of boron trifluoride, as has been formerly communicated[7].

Because in this reaction $\alpha$-pinene is isomerized to camphene by boron trifluoride ethyl ether complex and further is esterified[6], the isomerization of $\alpha$-pinene to camphene in the absence of glacial and anhydrous acetic acids was attempted. Namely, solutions of boron trifluoride ethyl ether complex in various solvents were prepared, $\alpha$-pinene was subjected to a reaction at room temperature with various amounts of catalyst and various reaction times, and the transformation of $\alpha$-pinene and the production of camphene were investigated, taking advantage of the infrared absorption spectrum and gas chromatography.

The determination of $\alpha$-pinene and camphene based on the infrared absorption spectrum has already been investigated by Kitajima, Takeshita et al.[8], who adopted 772 $cm^{-1}$ for $\alpha$-pinene and 667 $cm^{-1}$ for camphene as a characteristic absorption in the practice of estimation. The author adopted 1130 $cm^{-1}$ for $\alpha$-pinene and 1115 $cm^{-1}$ for camphene, made a calibration curve using $\alpha$-pinene purified by distillation, and diluted solutions of camphene 10~80 per cent, for which determination was carried out on the amount of $\alpha$-pinene and camphene in the reaction products catalyzed by boron trifluoride ethyl ether complex; at the same time, this result was compared with that of gas chromatography.

When a catalyst, boron trifluoride ethyl ether complex, was used with a solvent of ligroin or benzene, and also when it was directly applied to $\alpha$-pinene without the use of any solvents, violent heat generation and polymerization occurred, and the degree of heat generation and polymerization descending from ligroin through benzene to an absence of solvents.

When ethyl ether was used as a solvent, the generation of heat was hardly observed, and it was noted from the infrared absorption spectrum that by the action of boron trifluoride ethyl ether complex, $\alpha$-pinene is converted to camphene through the Wagner-Meerwein rearrangement and that the greater the extent of isomerization to camphene the larger the amount of boron trifluoride ethyl ether complex used and the longer the reaction time.

As the infrared absorption spectrum show peaks at 817 and 827 $cm^{-1}$, the existence of a group  is presumed, and hence the formation of polymers of $\alpha$-pinene is conceivable.

Reaction products in the solvent of benzene or ligroin for which no heat generation and polymerization appeared showed such infrared absorption spectra that, while the characteristic absorption (at 1130 $cm^{-1}$) was not observed, that for camphene was observed faintly at 1115 $cm^{-1}$ and those for end-methylene and *gem*-dimethyl radical were observed at 877 and 1660 $cm^{-1}$, and at 1363 and 1384 $cm^{-1}$ respectively. Gas chromatography of these reaction products showed a small peak corresponding to camphene; also in the case of solvents of benzene or ligroin, the formation of camphene was found, though in an extremely small amount.

In this reaction, the isomerization of $\alpha$-pinene into camphene by the action of boron

1) K. Ono, This Bulletin, 2, 16, 207 (1927).
2) T. Kuwada, *J. Soc. Chem. Ind., Japan, (Kōgyo Kwagaku Zasshi)*, 32, 1154 (1929).
3) E. Schwent and K. Schmidt, D. R. Pat. 578569 (1934).
4) P. A. Mulany, C., II, 430 (1931).
5) M. Berthelot, *Ann. chim. phys.*, (3) 38, 38 (1853).
6) I. G. Farbenindustrie, D. R. Pat. 589779 (1933).
7) K. Nagai, *Bull. Pharm. Kinki Univ.*, 3, 11 (1960).
8) M. Kitajima and T. Takeshita, *Report of the Central Research Institute, The Monopoly Corporation*, 95, 95 (1956).

trifluoride ethyl ether complex through the Wagner-Meerwein rearrangement was confirmed, and in the case of a violent reaction, although it almost polymerizes, the formation of a small amount of camphene was detected.

## Experimental

**Sample.** — α-Pinene and camphene purified by repeated distillation on metallic sodium were used. The physical constants of the samples are as follows: α-pinene b. p. 154.5~156°C, $d_4^{25}$ 0.8550, $n_D^{25}$ 1.4641; camphene b. p. 154~155°C, m. p. 47.0~47.5°C.

**The Calibration Curve of α-Pinene and Camphene.**—Camphene was diluted with α-pinene 10~80 per cent, and the characteristic absorption at 1130 and 1115 $cm^{-1}$ was selected for the infrared absorption spectra of α-pinene and camphene respectively; from the ratio of the above two absorptions, a calibration curve as seen in Fig. 1 was obtained.

Table I. Ratio of absorption at 1130 and 1115 $cm^{-1}$

| α-Pinene % $I_1$ | Camphene % $I_2$ | $\log I_1/I_2$ |
|---|---|---|
| 100 | — | 0.5090 |
| 90 | 10 | 0.6256 |
| 80 | 20 | 0.7238 |
| 70 | 30 | 0.8443 |
| 60 | 40 | 1.0164 |
| 50 | 50 | 1.222 |
| 40 | 60 | 1.411 |
| 30 | 70 | 1.644 |
| 20 | 80 | 1.905 |

$I_1$: The height of the mininum point on the absorption band of α-pinene
$I_2$: The height of the minimum point on the absorption band of camphene

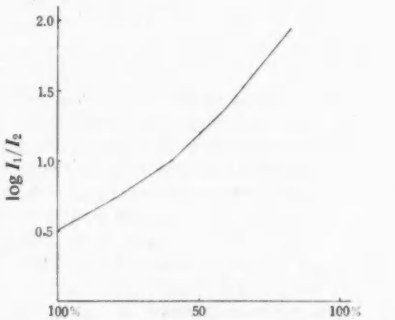



Fig. 1. Calibration curve of camphene and α-pinene.

**Reaction in the Solvent of Ethyl Ether.** — A mixture of α-pinene 10 ml. and ethyl ether 15 ml. was added to each 0.8, 1.5, 2.0 and 3.0 ml. of boron trifluoride ethyl ether complex and was allowed to react for 72 hr. at room temperature; after washing with 10% sodium carbonate and water, followed by drying, the reaction product was examined with the aid of the infrared absorption spectrum and gas chromatography. Figure 2 is the infrared absorption spectrum of the product obtained when α-pinene, camphene and 3.0 ml. of a catalyst were used. As shown from the calibration curve in Fig. 1, the yield of camphene is maximum, about 50 per cent, when 3.0 ml. of boron trifluoride ethyl ether complex was used, whereas in the reaction with 0.8 ml., the α-pinene remained almost unchanged.

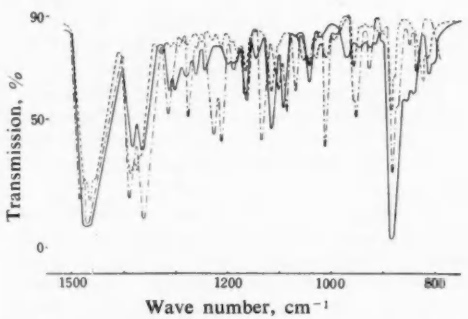



Fig. 2. Infrared absorption spectrum obtained by using α-pinene, camphene and 3.0 ml. catalyst.
——— Camphene ----- 3.0 ml. Catalyst
—·—· α-Pinene

Table II. Estimation of camphene on the basis of infrared absorption spectra of reaction products in ethyl ether

| Boron trifloride, ml. | Camphene % | Absorption coefficient |
|---|---|---|
| 0.8 | 10.0 | 0.529 |
| 1.5 | 41.0 | 1.029 |
| 2.0 | 46.2 | 1.127 |
| 3.0 | 50.0 | 1.214 |

Estimation of α-pinene and camphene based on gas chromatography

| Boron trifluoride, ml. | Camphene % | α-Pinene % |
|---|---|---|
| 0.8 | 12.1 | 80.9 |
| 1.5 | 44.2 | 29.7 |
| 2.0 | 44.0 | 16.9 |
| 3.0 | 52.9 | 10.6 |

P. E. G. 6000 (20 ml./min. 180°C, 0.25 kg./$cm^2$, 16 mV. 150 mA. 5 mm./min. He)

Moreover, the relation between the yield of camphene and the reaction time in the case of 3.0 ml. of boron trifluoride ethyl ether complex was investigated; the result is shown in Table III, from which it can be observed that a large amount of

TABLE III. RLATION BETWEEN THE YIELD OF CAMPHENE AND REACTION TIME

| | | | | |
|---|---|---|---|---|
| Infrared absorption spectrum | Reaction time, hr. | 24 | 48 | 72 |
| | Camphene % | 49.5 | 49.9 | 50.5 |
| | Absorption coefficient | 1.210 | 1.213 | 1.225 |
| Gas chromatography | Reaction time, hr. | 24 | 48 | 72 |
| | Camphene % | 50.9 | 51.2 | 51.5 |
| | $\alpha$-pinene, % | 12.8 | 12.4 | 10.6 |

camphene is formed in the case of an hour-long reaction.

**Reaction in the Solvent of Benzene and Ligroin.**—To 10 ml. of a sample, 15 ml. of both benzene and ligroin were added, and boron trifluoride ethyl ether complex was added to the benzene solution in amounts of 0.3, 0.5 and 1.0 ml. and to the ligroin solution in amounts of 1.5, 2.0 and 3.0 ml., and after reaction ceased, treatment similar to that described above was performed. In the case of these reactions, heat generation and polymerization occurred violently; when the amount of catalyst was small, the existence of camphene was observed, but $\alpha$-pinene was not, as shown from the data of the infrared absorption spectra and gas chromatography, although the estimation of the camphene formed was nevertheless difficult.

**Reaction Without Solvents.**—This reaction shows a remarkable heat generation and polymerization, yielding reddish-brown, viscous, oily substances; because the existence of $\alpha$-pinene was still observed only on the basis of the infrared absorption spectrum and gas chromatography, the estimation was not successful.

The author wishes to express her gratitude to Assistant Professor I. Ogura for his guidance and encouragement throughout this work, and her sincere thanks to Mr. K. Machida, Kyoto University, for his services in the measurement of the infrared absorption spectrum and to Mr. K. Matsushima of our University for his help in the analysis of gas chromatography.

*Pharmaceutical Faculty*
*Kinki University*
*Fuse-shi, Osaka*

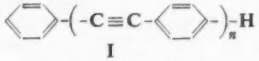
---

# *Alternant Conjugate Systems. I. Syntheses and Properties of Polytolans*

By Shōichi MISUMI

(Received March 7, 1961)

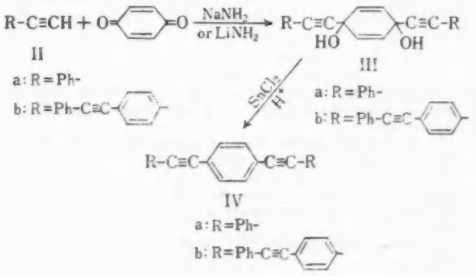
Alternative insertion of benzene nuclei between the triple bonds of the polyacetylenic chain of $\alpha,\omega$-diphenylpolyyne constitutes an interesting conjugate system, polytolan (I). The present author has investigated the syntheses of a series of polytolans (I; $n=2, 3, 4$) to compare their ultraviolet spectroscopic properties with those of polyphenylpolyene[1] and diphenylpolyacetylene.



I

The several methods[2-4] proposed for the synthesis of tolan all seem to be inadequate to the syntheses of the higher homologues owing to the poor solubility or the difficulty in the syntheses of the intermediates.

During the course of a study concerning the reaction of quinones with acetylenes, the author has found that polytolans having an even number of $n$ can be synthesized according to the following series of reactions. For example, the reaction of sodium phenylacetylide(IIa) in




1) S. Misumi and M. Kuwana, This Bulletin, **33**, 711 (1960).

2) L. I. Smith and M. M. Falkof, "Org. Synth.", **22**, 50 (1942); C. C. Price and C. E. Greene, *J. Polymer Sci.*, **6**, 111 (1952); G. Drefahl and G. Plötner, *Chem. Ber.*, **91**, 1280 (1958).

3) T. Curtius et al., ibid., **22**, 2161 (1889); *J. prakt. Chem.*, [2] **44**, 171 (1891); W. Schlenk et al., *Ann.*, **463**, 76 (1928).

4) P. Lipp, *Ber.*, **56**, 570 (1923); E. E. Harris et al., *J. Am. Chem. Soc.*, **48**, 3144 (1926); G. H. Coleman et al., ibid., **56**, 132 (1934); **58**, 2310 (1936).

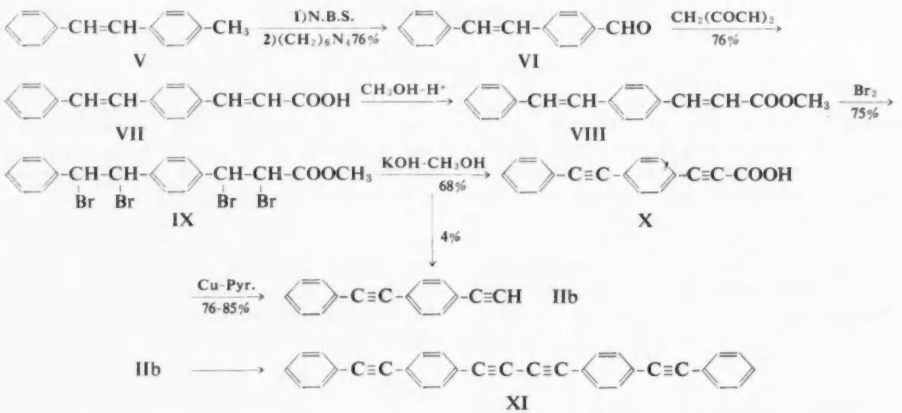
liquid ammonia with *p*-benzoquinone afforded the diacetylenic glycol (IIIa) in a yield of 31%. The reductive aromatization of IIIa with phosphorus diiodide or stannous chloride[5] resulted in the formation of distolan(IVa)[6]. Independently, IVa was synthesized by Ried according to essentially the same procedure[7]. The generalization of the reductive aromatization was achieved by his employing several kinds of quinones[7].

The present author has employed this method for the synthesis of tetrakistolan (I; $n=4$). The reaction of *p*-benzoquinone with the sodium salt of *p*-ethynyltolan (IIb) in liquid ammonia, in which IIb and its sodium salt are sparingly soluble, resulted in a recovery of the starting materials. As it was known that a lithium salt of an ethynyl compound has a larger solubility than a salt of other alkali metal[8], the reaction of the lithium salt of IIb with *p*-benzoquinone was carried out in dioxane, yielding tetra-acetylenic glycol(IIIb) in a yield of 13%. The reductive aromatization of IIIb afforded tetrakistolan (IVb) as light yellow needles with a green fluorescence. The solutions of IVb in various organic solvents exhibit an intense and characteristic violet fluorescence.

*p*-Ethynyltolan (IIb), which was used as a starting material for the synthesis of IVb, was synthesized according to the following series of reactions. A quantitative yield of the ester (VIII) was obtained by refluxing the suspension of *p*-styrylcinnamic acid (VII)[9] in methanol containing a catalytic amount of sulfuric acid. The dehydrobromination of the tetrabromide (IX) resulted in *p*-phenylethynyl-phenylpropiolic acid (X), together with a small amount of decarboxylated product (IIb). Several methods have been proposed for the decarboxylation of substituted phenylpropiolic acids[10-11], but the author has found that the acid (X) in pyridine or quinoline was smoothly decarboxylated to IIb in the presence of copper powder. Extension of the synthetic route of phenylacetylene[12] from cinnamic acid to styrylcinnamic acid (VII) was found to be unsuccessful owing to the poor solubility of the intermediate tetrabromide in various solvents.

*p*-Ethynyltolan (IIb) crystallizes in the form of colorless needles and gives amorphous yellow cuprous salt. Its mercuric acetylide was obtained in well-defined fine silky needles. As illustrated in Fig. 1, the ultraviolet spectrum of IIb was found to be closely related to tolan rather than to phenylacetylene, with a red-shift of ca. 15 mμ. The oxidative coupling of IIb according to Eglinton's method[13] afforded bis(*p*-phenylethynyl-phenyl)diacetylene (XI) as colorless plates. The disappearance of fine structure in the ultraviolet spectrum of XI as compared with that of diphenyldiacetylene is remarkable (Fig. 1).

Tristolan (I; $n=3$) was synthesized from




5) R. Kuhn et al., *Helv. Chim. Acta*, **11**, 87 (1928); *Ber.*, **71**, 783, 1510, 1889 (1938); **73**, 1410 (1940); *Chem. Ber.*, **84**, 566 (1951).

6) S. Misumi and M. Kuwana, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

7) W. Ried et al., *Chem. Ber.*, **90**, 2553 (1957); **91**, 2459 (1958); *Angew. Chem.*, **69**, 205, 614 (1957); *Naturwissenschaften*, **46**, 142 (1959).

8) B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, **1951**, 893.

9) G. Drefahl and W. Hartrodt, *J. prakt. Chem.*, [4] **276**, 124 (1957).

10) K. Schofield and J. C. Simpson, *J. Chem. Soc.*, **1945**, 512; H. Gilman et al., *J. Am. Chem. Soc.*, **53**, 4192 (1931); J. A. Leroy, *Bull. soc. chim. France*, [3] **7**, 644 (1892).

11) W. Weltzien and F. Micheel, *Ann.*, **433**, 247 (1923); M. M. Otto, *J. Am. Chem. Soc.*, **56**, 1393 (1934).

12) J. V. Nef, *Ann.*, **308**, 264 (1899); J. C. Hessler, "Org. Synth." Col. Vol., **I**, 438 (1948).

13) G. Eglinton and A. G. Galbraith, *Chem. & Ind.*, **1956**, 737; *J. Chem. Soc.*, **1959**, 889.

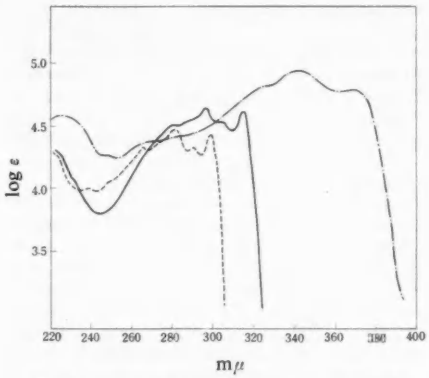



Fig. 1. The ultraviolet spectra of *p*-ethynyltolan (IIb, ——) and tolan (----) in *n*-hexane and bis(*p*-phenylethynylphenyl)-diacetylene (XI, —·—) in ethanol.

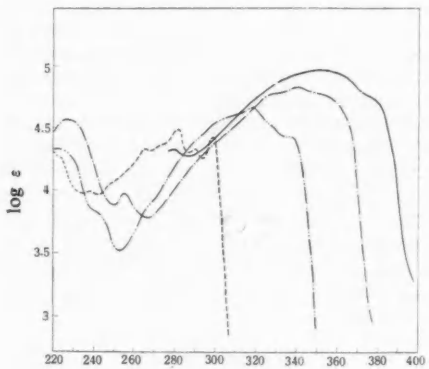



Fig. 2. The ultraviolet spectra of polytolans (I)
$n=4$, ——; $n=3$, —·—; $n=2$, ——; $n=1$, ----

*p,p'*-distyrylstilbene[14] according to the procedure of Drefahl[2].

The ultraviolet spectra and the physical properties of these polytolans are presented in Fig. 2 and Table I. An examination of the ultraviolet spectra of polytolans indicates that an increase in the length of the conjugate system causes a displacement of the strongest absorption band towards a longer wavelength; this bathochromic displacement, however, becomes smaller for each additional $-C_6H_4-C\equiv C-$ grouping. Two empirical formulae ($\lambda=kn+\lambda_0$ or $\lambda=k\sqrt{n}+\lambda_0$) have been proposed to relate the number of double bonds in a conjugated chromophore group ($n$) with the wavelength of the absorption maximum ($\lambda$)[15], but the absorption maxima of polytolans could not be expressed by either of these empirical formulae, because the plot of the wavelength of the absorption maxima against $n$ or the square root of $n$ does not give a straight line, as is illustrated in Fig. 3.

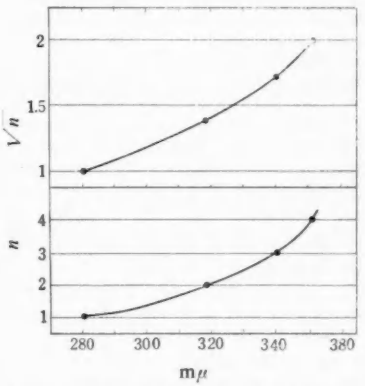



Fig. 3. Wavelength positions of the main absoption maxima plotted against number or $n\sqrt{n}$ of polytolans (I).

The spectra of tristolan (I; $n=3$) and tetrakistolan (I; $n=4$) showed absorption maxima at 256 and 279 mμ respectively. Similar maxima are also observed in the spectra of the corresponding ethylenic analogues. The occurrence of these bands can presumably be attributed to a higher order transition of the total chromophore, as is pointed out by Dale[16] and Zechmeister et al.[17].

The ultraviolet spectra of diphenylpolyacetylenes exhibit a regular bathochromic shift in accordance with the increase of the number of acetylenic linkage, also, the fine structure of the spectra becomes more and more distinct with the increase in the length of the conjugate system[18]. The same trend is also recognized in the case of diphenylpolyenes[19]. Kortüm attributed the increase in the fine structure of the spectra of diphenyl-polyyne and -polyene to the increase of the double bond character of single bonds in these conjugate systems. The increase in double bond character results

14) The synthesis of this substance will be reported on the following paper.

15) G. Schwarzenbach, *Z. Elektrochem.*, **47**, 40 (1941).
16) J. Dale, *Acta Chem. Scand.*, **8**, 1235 (1954).
17) L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár, and L. Pauling, *J. Am. Chem. Soc.*, **65**, 1940 (1943).
18) M. Nakagawa et al., *Proc. Japan Acad.*, **26**, 38, 43 (1950); *J. Chem. Soc. Japan, Pure. Chem. Sec.* (*Nippon Kagaku Zasshi*), **71**, 561, 993 (1951); H. H. Schlubach and V. Franzen, *Ann.*, **573**, 110 (1951); F. Bohlmann, *Chem. Ber.*, **84**, 785 (1951); **86**, 63 (1953); *Angew. Chem.*, **65**, 385 (1953).
19) K. W. Haussen, R. Kuhn and A. Smakula, *Z. physik. Chem.*, **B 29**, 384 (1935).

Table I. Properties of polytolans and related compounds

| | M.p., °C | Fluorescence | | UV spectrum | |
|---|---|---|---|---|---|
| | | Solid | Solution | $\lambda_{max}$, mμ | Solvent |
| Distolan(I : $n$=2) | 181.5~182 | — | Light violet | 222, 318, 337 | a |
| Tristolan(I : $n$=3) | 283 ~285 | Light green | Violet | 226, 256, 325*, 340 | c |
| Tetrakistolan(I : $n$=4) | 307 ~312 | Light green | Intense violet | 279, 351, 378* | b |
| $p$-Ethynyltolan(IIb) | 90.5~91 | — | — | 279, 288*, 295, 303, 314 | a |
| (XI) | 229 ~229.5 | — | Violet | 225, 268*, 326*, 342, 368 | d |

* inflexion ; a : $n$-hexane, b : benzene, c : chloroform, d : 95% alcohol

in a fixation of the molecule in a uniplanar conformation and necessarily retards the torsional vibration of the molecule[20].

On the contrary, the fine structure in the spectra of polytolans gradually becomes obscure with the increase in the length of the alternant conjugate system. The distinct fine structure observed in the spectrum of tolan can be traced in that of distolan (IVa), but the spectra of tris- and tetrakis-tolan show only a weak inflection at the corresponding positions, as is illustrated in Fig. 2. The single bond length of the $C_6H_5$–C≡ grouping has been reported to be almost identical in the series of diphenylpolyyne, whereas a distinct contraction of the single bond length inserted between two acetylenic linkages was observed in the same series, as

Table II. Single bond lengths in diphenylpolyyne Ph–(C≡C)$_n$–Ph

| $n$ | Bond length of Ph–C≡ Å | Bond length of ≡C–C≡ Å | Ref. |
|---|---|---|---|
| 1 | 1.40 | — | 21 |
| 2 | 1.44 | 1.39 | 22 |
| 4 | 1.42 | 1.37, 1.33, 1.37 | 23 |
| 5 | 1.45 | 1.39, 1.33, 1.33, 1.39 | 23 |

is summarized in Table II. These results indicate that the single bond in the $C_6H_5$–C≡ grouping has a minor degree of multiple bond character as compared with the single bond in ≡C–C≡ grouping. Consequently, an insertion of the $p$-phenylene group in a position of single bond in a conjugate polyyne chain may cause an increase of torsional vibration about the single bond of the ≡C–$C_6H_4$–C≡ grouping. Also, the increase in the number of single bond with a minor multiple bond character may increase the transition energy of photoexcitation. The disappearance of the fine structure and the hypsochromic shift of absoption maxima in the spectra of polytolans as compared with those of diphenylpolyynes seem to be attributable to the above-mentioned two reasons. This inference is also cosistent with the fact that $p$-ethynyltolan and tolan show quite similar absorption curves (Fig. 1) and the fact that the fine structure which is observed in the spectrum of diphenyldiacetylene is almost lost in the absorption curve of bis($p$-phenylethynyl-phenyl)diacetylene (XI) (Fig. 1).

The ultraviolet spectrum of distolan reported by Drefahl[2] showed a strong inflection at ca. 350 mμ which could not be observed in the spectrum of the compound prepared by the author. The presence of inflection at this wavelength seems to arise from a contamination with the starting material, $p$-distyrylbenzene ($\lambda_{max}$ 350 mμ) or $p$-styryltolan ($\lambda_{max}$ 333; $\lambda_{infl.}$ 352 mμ).

## Experimental*

**1, 4-Bisphenylethynyl-2, 5-cyclohexadien-1, 4-diol (IIIa).**—To a solution of sodium amide (prepared from sodium, 3.8 g., 0.167 mol.) in liquid ammonia (100 ml.) was added dropwise phenylacetylene (17 g., 0.167 mol.) in dry ether (50 ml.). After stirring for 2 hr., $p$-benzoquinone (10 g., 0.093 mol.) in dry tetrahydrofuran (70 ml.) was dropped into the mixture over a period of 3 hr. A transient development of blue color was observed on the addition of the quinone, and the entire mixture gradually changed to a deep brown solution. Ammonia was evaporated after the addition of ammonium chloride, and the residual solid was extracted with ethyl acetate. The extract was thoroughly washed with water and dried. After removal of the solvent, the residue was dissolved in ethyl acetate-benzene and passed through a short column of alumina. The crude crystals obtained on concentrating the solvent were recrystallized from benzene to give IIIa, colorless leaflets, m. p. 176~177°C, yield 8.1 g. (31.2%). (Ried[7] reported a yield of 50~55% employing lithium amide.)

Found : C, 84.47 ; H, 5.04. Calcd. for $C_{22}H_{16}O_2$ : C, 84.59 ; H,5.16%.

20) G. Kortüm and G. Dreesen, *Chem. Ber.*, **84**, 182 (1951).
21) J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, **A 164**, 436 (1938).
22) E. H. Wiebenga, *Z. Krist.*, **102**, 193 (1940).
23) T. Watanabe, N. Masaki and H. Mitsuda, International Congress of the International Union of Cristallography, Cambridge, England, Aug., 1960.

* All melting points are uncorrected.

IR max($cm^{-1}$) 3320, 3260($\nu_{OH}$), 2225($\nu_{C\equiv C}$), 1007($\delta_{OH}$).

***p*-Bis(phenylethynyl)benzene [Distolan] (I : n=2)**—A solution of stannous chloride dihydrate (1.0 g.) in concentrated hydrochloric acid (3.0 ml.) was added to a stirred solution of the glycol (IIIa, 388 mg.) in tetrahydrofuran (20 ml.), and the mixture was stirred for several hours at room temperature. After standing overnight, the reaction mixture was poured into water and extracted with benzene. The extract was washed with water and dried. After removal of the solvent, the residue was dissolved in light petroleum-benzene (1 : 1, 10 ml.). The solution was then chromatographed over alumina and eluted with the same solvent, resulting in crude crystals. This was recrystallized from dry ethanol, yielding IVa, m. p. 172~175°C, 115 mg. (33.1%). Sublimation of this material in vacuo (160~175°C/15 mmHg) afforded pure IVa, colorless needles.

Found: C, 95.12; H, 5.12. Calcd. for $C_{22}H_{14}$: C, 94.93; H, 5.07%.

IVa was also obtained in a yield of ca. 20% by a reductive aromatization of IIIa with phosphorus diiodide.

***p*-Bis(β-phenylethyl)benzene.**—IVa in dry tetrahydrofuran was catalytically reduced over palladium-charcoal (5%). After removal of the catalyst, the reduction product obtained by evaporating the solvent was recrystallized twice from ethanol to yield *p*-bis(β-phenylethyl)benzene, on colorless plates, m. p. 90.5~91°C.

Found: C, 92.59; H, 7.67. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74%.

***p*-Stilbenealdehyde(VI).**—VI was prepared according to the procedure of Drefahl[9] with slight modifications, m. p. 113~114°C., 76% yield (lit. value, m. p. 116~117°C.).

IR max.($cm^{-1}$) 1695($\nu_{C=O}$), 1205, 1165(-CHO), 968($\delta_{=CH-}$).

***p*-Styrylcinnamic Acid (VII).**—Stilbenealdehyde (VI, 30.2 g., 0.145 mol.) and malonic acid (31 g., 0.29 mol.) were dissolved in a mixture of pyridine (60 ml.) and piperidine (1.5 ml.). A vigorous evolution of carbon dioxide was observed when the solution was warmed to 60~65°C. The solution was kept at 100°C for 3 hr. and then refluxed for 2 hr. The cooled reaction mixture was poured onto crashed ice (300 g.) containing hydrochloric acid (100 ml.). The precipitate was then filtered and washed with water. Recrystallization of this material from acetic acid yielded VII, on lustrous light yellow plates, m. p. 255~256°C, 27.5 g. (76%) (lit. value, m. p. 256~258°C, 70%)[9].

IR max.($cm^{-1}$) 1685($\nu_{C=O}$), 1427, 1278(-COOH), 959($\delta_{=CH-}$).

**Methyl *p*-Styrylcinnamate (VIII).**—A few milliliters of concentrated sulfuric acid was added to a suspension of styrylcinnamic acid (VII, 20 g.) in methanol (600 ml.), and the mixture was refluxed for 10 hr. The crystals of the acid gradually changed to pale greenish yellow plates. The cooled reaction mixture was then filtered. The crystals obtained by concentrating the filtrate were combined with the first crop and recrystallized from carbon tetrachloride, resulting in VIII, on light yellow plates, m. p. 185.5~186°C, 20.4 g. (97%).

Found: C, 81.79; H, 6.18. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

UV max(mμ) 236(ε=8,000), 345(24,000)(in 95% ethanol)

IR max($cm^{-1}$)1717($\nu_{C=O}$), 1169, 1114(-$COOCH_3$), 980, 969, 961($\delta_{=CH-}$).

**Methyl *p*-Styrylcinnamate Tetrabromide (IX).**—Bromine (30.0 g., 0.19 mol.) in chloroform (30 ml.) was gradually added to a stirred solution of the ester (VIII, 20.4 g., 0.077 mol.) in chloroform (700 ml.) under cooling with running water. The large amount of crystals deposited made the agitation of the reaction mixture impossible after about two-thirds of bromine had been added. After all the bromine had been introduced, the mixture was warmed to 40°C to complete the reaction. The crystals were filtered and washed with a small amount of chloroform, yielding the tetrabromide, 33.8 g. (75%), m. p. 235~238°C (decomp.). Further recrystallization from acetic acid afforded a pure material, colorless scale-like crystals, m. p. 242°C (decomp.).

Found: Br, 54.25. Calcd. for $C_{18}H_{16}O_2Br_4$: Br, 54.74%.

***p*-Phenylethynyl-phenylpropiolic Acid (X).**—The tetrabromide (IX, 34 g., 0.058 mol.) was intimately mixed with finely powdered potassium hydroxide (90 g., 0.6 mol.) and absolute methanol (400 ml.) was added in one portion to the mixture. After the vigorous reaction had ceased, the mixture was refluxed for 8 to 10 hr. The cooled reaction mixture was poured into water (600 ml.), and the potassium .propiolate deposited was filtered and washed with a small amount of water. The combined filtrate and washing were extracted with ether. The ethereal extract was washed with water and dried. The residue obtained by removing the solvent was dissolved in light petroleum (b. p. 60~70°C.) and passed through a short column of alumina. Recrystallization of the crude crystals which were obtained by concentrating the filtrate gave IIb, pale yellow needles, 0.5 g. (4.3 %), m. p. 87~89.5°C.

The above-mentioned potassium salt was dissolved in hot methanol (400 ml.) and treated with active charcoal. On acidification of the methanolic solution with concentrated hydrochloric acid, crude *p*-phenylethynyl-phenylpropiolic acid (X) was obtained as crystals, m. p. 200~203°C, 9.7 g. (68%). Further purification was carried out by repeating the precipitation of the acid (X) from the methanolic solution with the addition of water, while a decomposition was observed when a solution of the acid is heated, especially in the presence of active charcoal. The pure material melts at 206~207°C.

Found: C, 82.67; H, 4.15. Calcd. for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09%.

IR max. ($cm^{-1}$) 2205($\nu_{C\equiv C}$), 1667($\nu_{C=O}$), 1440, 1295(-COOH).

***p*-Ethynyltolan (IIb).**—To a solution of the propiolic acid (X, 1 part) in pyridine (10 parts) was added copper powder (0.1 part). The evolution of carbon dioxide was observed immediately, and in a few minutes the reaction mixture began

to froth vigorously. After the vigorous reaction had subsided, the mixture was refluxed for 40~60 min. To the cooled reaction mixture was added light petroleum (b. p. 60~70°C), and copper powder was removed by filtration. The filtrate was washed repeatedly with 2 N hydrochloric acid and then with aqueous sodium hydroxide and water successively. Concentration of the dried filtrate resulted in light brown needles, m. p. 78~83°C (yield, 76~85%). The crude ethynyltolan thus obtained was purified through chromatography over alumina, as the crude material was contaminated with a small amount of the propiolic ester. Recrystallization of the eluate from light petroleum gave pure IIb.

Found: C, 94.72; H, 4.98. Calcd. for $C_{16}H_{10}$: C, 95.02; H, 500%.

IR max.($cm^{-1}$) 3260($\nu_{\equiv CH}$).

The mercuric acetylide which was prepared according to the method of Johnson[24] was recrystallized from ethanol-benzene, yielding silky long needles, m. p. 244~245°C.

IR max.($cm^{-1}$) 2150 ($\nu_{C\equiv C}$).

**Bis(*p*-phenylethynyl-phenyl)diacetylene (XI).**—Cupric acetate monohydrate (7.5 g.) was added to a solution of *p*-ethynyltolan (IIb, 0.5 g.) in dry pyridine (50 ml.). The mixture was stirred for 8 hr. at 60~75°C. The reation mixture was diluted with benzene (200 ml.) and washed with 2 N hydrochloric acid, aqueous sodium hydroxide and water successively. The benzene solution was dried and the solvent removed, yielding a red solid. The crude material was washed twice with a small amount of light petroleum. The light yellow crystals thus obtained were recrystallized twice from benzene to give pure XI, on colorless plates.

Found: C, 95.04; H, 4.61. Calcd. for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

**1, 4-Bis(*p*-phenylethynyl-phenylethynyl)-2, 5-cyclohexadien-1, 4-diol (IIIb).**—Dry dioxane (50 ml.) was added to a solution of lithium amide (prepared from lithium, 0.1 g., 14.3 mmol.) in liquid ammonia, and the ammonia was evaporated, resulting in a light pink solution. Into this solution was stirred *p*-ethynyltolan (IIb, 3 g., 14.8 mmol.) in dry dioxane (10 ml.). The color of the solution gradually changed from yellow to a transparent dark brown. After warming to 50°C for 20 min., the mixture was refluxed for 10 min. to expel the remaining ammonia and then cooled to room temperature. Under vigorous stirring, a solution of *p*-benzoquinone (0.8 g., 7.5 mmol.) in dry dioxane (20 ml.) was slowly added to the mixture over a period of 4 hr. A transient development of blue color was observed, and the color of the mixture changed to brown, forming a large amount of precipitate. The reaction mixture was stirred for ca. 20 hr. at room temperature and then refluxed for 3 hr. The cooled reaction mixture was introduced into water (500 ml.) and extracted with ethyl acetate. The extract was washed with water, dried and chromatographed over alumina. The crystalline fractions were recrystallized from benzene, yielding the glycol (IIIb), in the form of fine, long silky needles, m. p. 248~250°C., 475 mg. (12.6%).

Found: C, 88.90; H, 4.72. Calcd. for $C_{38}H_{24}O_2$: C, 89.04; H, 4.72%.

IR max.($cm^{-1}$) 3580, 3460($\nu_{OH}$), 2230($\nu_{C\equiv C}$), 1025, 1000 ($\delta_{OH}$).

**1, 4-Bis (*p*-phenylethynyl-phenylethynyl) benzene [Tetrakistolan] (IVb).**—To a warm solution of the glycol (IIIb, 245 mg.) in ethyl acetate (30 ml.) was added a solution of stannous chloride dihydrate (1 g.) in acetic acid (2 ml.) and ethyl acetate (2 ml.). The immediate deposition of a light yellow precipitate was observed. The mixture was then refluxed for 4 hr. and cooled. The precipitate was filtered (172 mg.) and dissolved in ethyl acetate. The solution was passed through a short column of alumina, and the filtrate was dried by evaporation. The residue, after recrystallization from chlorobenzene, gave tetrakistolan (IVb), in the form of light greenish yellow needles with a green fluorescence.

Found: C, 95.06; H, 4.81. Calcd. for $C_{38}H_{22}$: C, 95.37; H, 4.63%.

The author wishes to express his hearty thanks to Professor Masazumi Nakagawa for his helpful guidance throughout this work. The cost of this research was partly defrayed from the Scientific Research Expenditure of the Ministry of Education, to which author's thanks are also due.

*Department of Chemistry*
*Faculty of Science*
*Osaka University*
*Kita-ku, Osaka*

24) J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).

# *Alternant Conjugate Systems. II. Syntheses of Stereoisomeric p-Distyrylbenzenes and Related Compounds**

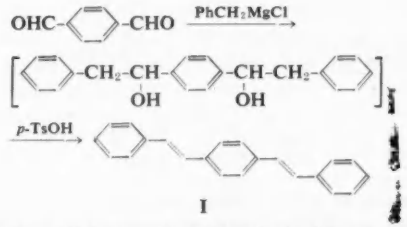
By Sōichi MISUMI, Motoyuki KUWANA, Kunie MURASHIMA and Masazumi NAKAGAWA

(Received March 7, 1961)

From a study of the ultraviolet absorption spectra of cis-trans isomeric carotenoids, Zechmeister and Pauling[1] have proposed a so-called "cis-peak rule" to correlate the molecular geometry with the spectrum. But the ultraviolet spectra of 1, 18-diphenyl-3, 7, 12, 16-tetramethyl-octadecanonaenes containing one or two sterically hindered cis-double bonds lack the cis-peak[2] which would be expected to appear according to the prediction of Zechmeister. Oroshnik[3] has also pointed out from his study of the ultraviolet spectra of sterically hindered retrovitamin A methyl ether and analogous compounds that the validity of Zechmeister's rule may be restricted to sterically unhindered cis-polyenes and that the spectra of hindered cis-polyenes cannot be explained by this rule alone.

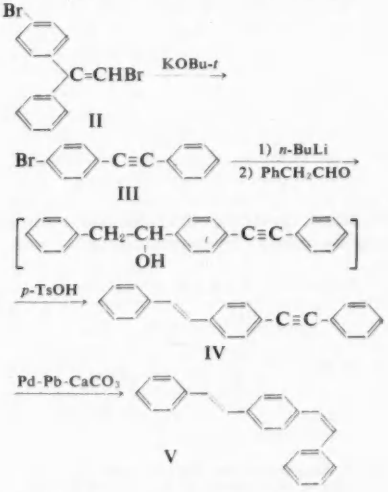
In order to examine the validity of Zechmeister's rule with regard to stilbene derivatives containing hindered cis-double bonds, the authors have carried out the syntheses of three stereoisomers of *p*-distyrylbenzene and related compounds. The present paper deals with the syntheses of these compounds; their spectroscopic properties will be discussed together with those of *p, p'*-distyrylstilbenes and related compounds in the following paper of this series.

Among the three possible geometrical isomers of *p*-distyrylbenzene, the trans, trans-isomer was prepared by Kaufmann as early as 1917[4]. Afterward, various methods of preparation of this compound have been proposed[5]. The present authors have synthesized the trans-trans compound I according to the following series of reactions.




I

It is well-known that the ethylenic compound obtained by a dehydrohalogenation or dehydration reaction contains only a small amount of cis-isomer and that the partial hydrogenation of an acetylenic compound over Lindlar's catalyst is regarded as the most practical method obtaining cis-ethylenic compound[6]. More recently, it has been reported in some cases that the Wittig reaction[7] affords cis-compound together with trans-isomer. The authors have found during the course of the synthetical studies of stilbene homologues that the Wittig reaction is feasible for the synthesis of cis-isomer. Therefore, the second isomer, the *trans, cis-p*-distyrylbenzene (V), was prepared by the above-mentioned two methods.




* For a preliminary announcement of this study, see This Bulletin, 33, 711 (1960).

1) L. Zechmeister, L. Pauling et al., *J. Am. Chem. Soc.*, 65, 1940 (1943); L. Zechmeister, *Chem. Revs.*, 34, 267 (1944); *Experientia*, 10, 1 (1954).

2) C. F. Garber, C. H. Eugster and P. Karrer, *Helv. Chim. Acta*, 35, 1580 (1952); 36, 562 (1953).

3) W. Oroshnik and A. D. Mebane, *J. Am. Chem. Soc.*, 76, 5719 (1954).

4) H. Kaufmann, *Ber.*, 50, 524 (1917).

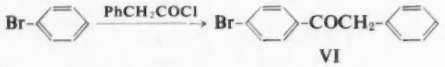
5) a) G. Drefahl and G. Plötner, *Chem. Ber.*, 91, 1274 (1958); b) J. Dale, *Acta Chem. Scand.*, 11, 971 (1957); c) K. Friedrich and H. G. Henning, *Chem Ber.*, 92, 2944 (1959); T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, 24, 1246 (1959).

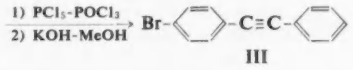
6) H. Lindlar, *Helv. Chim. Acta*, 35, 446 (1952).

7) G. Wittig, *Angew. Chem.*, 71, 260 (1959).

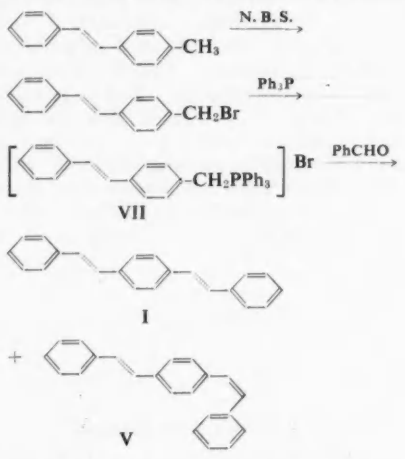
The corresponding acetylenic analogue, *p*-styryltolan (IV), was synthesized according to the following scheme from *p*-bromotolan (III), which is prepared by means of a Fritsch-Buttenberg-Wiechell rearrangement[8] of *α*-*p*-bromophenyl-*β*-bromostyrene (II).

*p*-Bromotolan (III) was also obtained by a dehydrochlorination of the ketodichloride of *p*-bromodesoxybenzoin (VI). This method has, however, been found to be less advantageous owing to the low yield of the Friedel-Crafts reaction for the preparation of VI.

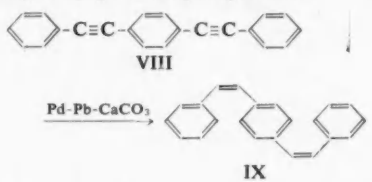


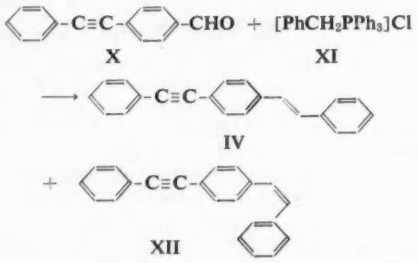

*p*-Bromomethylstilbene which was derived from *p*-methylstilbene was converted to phosphonium salt VII. The reaction of the salt VII with benzaldehyde yielded *trans*, *trans*-distyrylbenzene and *trans*, *cis*-distyrylbenzene (V) in about the same yield. The trans, cis-isomer V thus obtained was found to be identical




with the trans, cis-isomer derived from acetylenic analogue by partial hydrogenation.




The third isomer, *cis*, *cis*-*p*-distyrylbenzene (IX), was prepared by the double partial hydrogenation of *p*-bisphenylethynyl-benzene (VIII)[9] over Lindlar's catalyst*.




The reaction of tolanaldehyde (X)[10] with benzyltriphenylphosphonium chloride (XI) also gave *trans*-*p*-styryltolan (IV) and *cis*-*p*-styryltolan (XII) in about equal yields. The formation of an equal amount of cis-isomer was also observed in the Wittig reaction of other stilbene homologues, which experiments will be reported on in a following paper. The formation of a four-membered cycle in an intermediate stage of Wittig reaction is generally accepted, and the formation of cis- and trans-isomers in an almost equal yield seems to be rather peculiar on the basis of this hypothesis, since the intermediate of the cis-isomer is

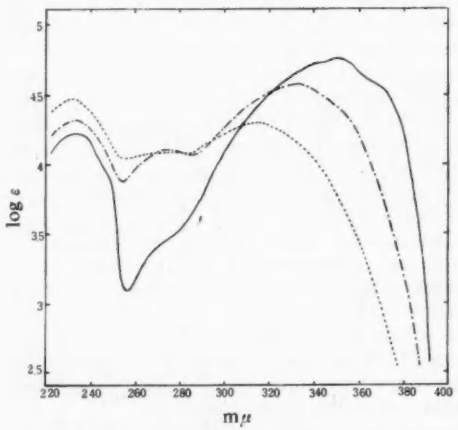



Fig. 1. The ultraviolet spectra of *p*-distyrylbenzenes in *n*-hexane.
*trans*, *trans*, ——; *trans*, *cis*, —·—·; *cis*, *cis*, ----

8) W. P. Buttenberg, *Ann.*, **279**, 327 (1894); P. Lipp, *Ber.*, **56**, 570 (1923); G. H. Coleman et al., *J. Am. Chem. Soc.*, **56**, 132 (1934); **58**, 2310 (1936); M. Bouis, *Ann. Chim.*, [10] **9**, 402 (1928); A. A. Bothner-By, *J. Am. Chem. Soc.*, **77**, 3293 (1955).

9) S. Misumi, This Bulletin, **34**, 1827 (1961).

* Dale[5a] assigned the configuration of *trans*, *cis*-distyrylbenzene to a compound of m.p. about 95°C., which was isolated from the products of the photo-isomerization of trans, trans-isomer. However, the ultraviolet spectra of pure trans, cis- and cis, cis-compounds indicate that the compound of m.p. about 95°C is possibly a mixture of trans, cis- and cis, cis-isomers.

10) G. Drefahl and G. Plötner, *Chem. Ber.*, **93**, 990 (1960).

TABLE I. PROPERTIES OF *p*-DISTYRYLBENZENES AND RELATED COMPOUNDS

| | M. p., °C | UV spectrum, $\lambda_{max}(\varepsilon_{max})$, mμ | | | |
|---|---|---|---|---|---|
| *t*—*t* | 266 ~267 | 232 (16200) | | 350 (57000) | |
| *t*—*c* | 114 ~114.5 | 232 (20000) | 273 (12200) | 331 (36500) | |
| *c*—*c* | 86.5~ 87.5 | 232 (27600) | 270 (10900) | 314 (17700) | |
| A—A | 181.5~182 | 222 (20800) | | 318 (45400) | 337 (27000) |
| A—*t* | 211 ~211.5 | 230 (26600) | | 333 (55300) | |
| A—*c* | 78 ~ 78.5 | 227 (26800) | 271 (17700) | 312 (32900) | |

*t*, *c* and A denote *cis*-ethylenic, *trans*-ethylenic and acetylenic linkage, respectively.

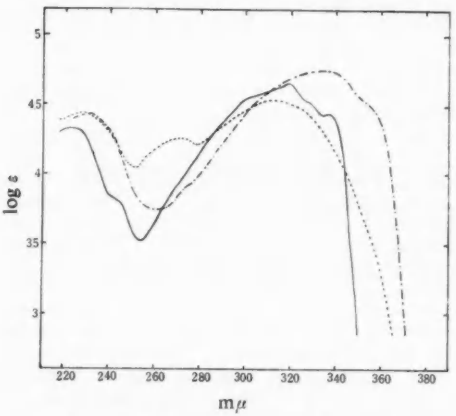



Fig. 2. The ultraviolet spectra of *p*-styryltolans (IV, *trans*, —·—·; XII, *cis*, ----) and distolan (VIII, ——) in *n*-hexane.

probably less stable than that of the trans-isomer owing to the steric interaction of two phenyl groups.

The ultraviolet spectra of the above-mentioned three stereoisomeric *p*-distyrylbenzenes and two *p*-styryltolans are presented in Figs. 1 and 2. The spectroscopic and physical properties of these compounds are summarized in Table I.

The shifts of the wavelength, where the absorption maxima of these compounds at the longest wavelength appear, represent an interesting feature. The introduction of a cis-double bond or an acetylenic bond instead of a trans-double bond caused a blue shift of ca. 18 and 16 mμ respectively. The absorption intensities of $\lambda_{max}$ at the longest wavelength of *trans*-*trans*, *trans*-acetylene and acetylene-acetylene compounds diminish with the increase in the amount of acetylenic linkage. Usually the absorption intensity of polyyne compound was found to be 2.6 fold as large as that of polyene compound. This phenomenon has been explained in terms of the larger number of π-electrons in triple bond and the linear geometry of polyyne compound[11]. As stated above, this is not valid for the absorption intensities of an alternant conjugate system of the styryltolan type. The decrease of absorption intensity by the introduction of aceylenic linkage seems to be attributable to an enhancement of the free rotation of the *p*-phenylene group, which may decrease the probability of transition of the full conjugate system.

The photoisomerizations and the discussions concerning the cis-peak of these compounds will be reported in the following paper together with those of the compounds of the distyrylstilbene series.

11) F. Bohlmann, *Angew. Chem.*, **65**, 385 (1953).

## Experimental*

***trans*, *trans*-*p*-Distyrylbenzene (I).**—*a) From Terephthalaldehyde.*—To a stirred solution of benzylmagnesium chloride (from magnesium, 3.75 g. and benzyl chloride, 20.0 g., 0.158 mol.) in dry ether (100 ml.) was added dropwise terephthalaldehyde[12] (10.0 g., 0.075 mol.) in dry tetrahydrofuran (150 ml.); this mixture was refluxed for 3 hr. A saturated aqueous solution of ammonium chloride was added to the cooled mixture and the organic layer separated by decantation. The inorganic residue was extracted with ether and the extract combined with the organic layer. The solvent was distilled from the combined solution to give the crude glycol (27 g.). A solution of the crude glycol (25 g.) in dry toluene (220 ml.) containing *p*-toluenesulfonic acid (0.8 g.) was refluxed for 2 hr. The crystals deposited from the cooled reaction mixture were filtered and recrystallized from chlorobenzene, yielding *trans*, *trans*-*p*-distyrylbenzene (I), on light greenish yellow plates, m. p. 261~262.5°C. The viscous tarry material obtained by concentration of the mother liquor was treated with chlorobenzene, yielding a second crop of I. The crude material was repeatedly recrystallized from chlorobenzene to give I. The total yield was found to be 4.3 g. (22%). Further recrystallization from the same solvent afforded pure I, m. p. 266~267°C.

Found: C, 93.59; H, 6.76. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

*b) From p-Styrylbenzyl-triphenylphosphonium Bromide (VII).*—I was obtained from VII together with *trans*, *cis*-*p*-distyrylbenzene (V). The details will be described in section b) on the preparation of V.

***p*-Bromotolan (III).**—The bromostyrene (II) was prepared from *p*-bromoacetophenone[13] via three

* All melting points are uncorrected.

12) J. M. Snell and A. Weissberger, "Org. Synth.", Col. Vol. I (1948), p. 109.

13) R. Adams and C. R. Noller, ibid., (1955), p. 788.

steps according to the method of Bothner-By[9] in a yield of 26%, trans-form, m. p. 105.5~106.5°C. A solution of potassium *tert*-butoxide in *tert*-butyl alcohol (from potassium, 3 g. and *tert*-butyl alcohol, 40 ml.) was stirred with the finely powdered *p*-bromostyrene (II, 17 g., 0.05 mol.), and the mixture was refluxed for 3 days. To the cooled reaction mixture, *tert*-butyl alcohol (180 ml.) and water (360 ml.) were added, precipitating a colorless solid. The solid was filtered, washed with water and dried. The recrystallization of solid from light petroleum yielded III, in the form of colorless plates, m. p. 82~83°C, 10.5 g. (83%).

Found: C, 65.81; H, 3.54; Br, 30.73. Calcd. for $C_{14}H_9Br$: C, 65.39; H, 3.53; Br, 31.07%.

***trans-p*-Styryltolan (IV).**—*a) From p-Bromotolan (III).*—A little excess of *n*-butyllithium in ether (prepared from *n*-butyl chloride and lithium, the concentration being estimated by titration with 0.1 N hydrochloric acid) was slowly stirred into a solution of *p*-bromotolan (10.3 g., 0.04 mol.) in dry ether (100 ml.) in an atmosphere of pure nitrogen, and the mixture was refluxed for 2.5 hr. To the resultant orange yellow solution of tolan-lithium was added phenylacetaldehyde (6 g., 0.05 mol., freshly prepared from the dimethylacetal) in dry ether (65 ml.) at room temperature. A gradual change of the orange yellow color of the mixture to a white suspension was observed. Then the mixture was refluxed for 3 hr. to complete the reaction. A slow stream of pure nitrogen was introduced continuously into the reaction flask throughout these operations. A saturated aqueous solution of ammonium chloride (5.5 g.) and water were successively added to the cooled reaction mixture. The organic layer was separated. The organic layer and the ethereal extract were combined, washed with water and dried. The orange-colored oily residue obtained on evaporating the solvent was dissolved in dry toluene (150 ml.) containing *p*-toluenesulfonic acid (0.5 g.). The solution was refluxed, and the water formed was removed continuously by means of a water-separator. The crystals deposited on cooling the mixture were filtered and the mother liquor concentrated, resulting in the deposition of a second crop of crystals. The combined crystals were recrystallized twice from benzene, yielding *trans-p*-styryltolan, in the form of colorless leaflets, m. p. 211~211.5°C, 3.5 g. (31%).

Found: C, 94.09; H, 5.83. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75%.

*b) From p-Tolanaldehyde (X) by Wittig Reaction.*—The reactions described below were carried out in a dark place. *p*-Tolanaldehyde[10] (1 g., 4.85 mmol.) and benzyltriphenylphosphonium chloride (2 g., 5.15 mmol., m. p. 313~315°C) were mixed with absolute ethanol (25 ml.). To the stirred suspension was added an excess of lithium ethoxide in absolute ethanol. After stirring for 8.5 hr. at room temperature, the deposited pale yellow solid (0.7 g., a mixture of *trans-p*-styryltolan and phosphonium salt) was filtered. The solid was dissolved in benzene and the solution passed through a column of alumina to remove the phosphonium salt. The crude crystals obtained on evaporating the filtrate were recrystallized from benzene, yielding *trans-p*-styryltolan, in the form of colorless leaflets, m. p. 210~211°C, 0.5 g. (35.7%); this was found to be identical with the specimen obtained by the above-mentioned method a) by mixed melting point determination.

***cis-p*-Styryltolan (XII).**—The following operations were carried out in a dark place. The above-mentioned mother liquor of the Wittig reaction was diluted with water, precipitating a mixture of a solid and a brown oily material. The precipitate was dissolved in light petroleum. The solution was passed through a column of alumina and eluted with the same solvent. A colorless solid (m. p. 76~78°C) obtained from the eluate was recrystallized from aqueous ethanol, giving *cis-p*-styryltolan (XII), m. p. 78~78.5°C, colorless needles, 0.6 g. (49.2%).

Found: C, 93.88; H, 5.69. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75%.

***trans, cis-p*-Distyrylbenzene (V).**—*a) Partial Reduction of trans-p-Styryltolan (IV).*—The following operations were carried out in a dark place. Hydrogenation of the styryltolan (IV, 0.1 g.) in tetrahydrofuran (20 ml.) over Lindlar's catalyst resulted in the uptake of ca. 1 mol. of hydrogen. After removal of the catalyst, the solvent was evaporated under a reduced pressure. The residue was mixed with hot ethanol. The hot mixture was filtered to remove a small amount of insoluble trans, trans-isomer. The crystals separated on cooling the filtrate were filtered promptly. The crystals were found to be pure trans, cis-isomer V, in the form of colorless plates, m. p. 114~114.5°C.

Found: C, 93.58; H, 6.44. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

*b) From p-Styrylbenzyl-triphenylphosphonium Bromide (VII).*—The following reactions and operations were carried out in a dark place. The phosphonium salt (VII, 2 g., 3.74 mmol.) was added to a solution of benzaldehyde (0.4 g., 3.77 mmol.) in absolute ethanol (60 ml.). Into this suspension was stirred an excess of a solution of lithium ethoxide in absolute ethanol. The mixture was stirred for 3 hr. at room temperature, and the solid was filtered (filtrate A). The solid was digested with boiling ethanol (30 ml.) and the insoluble material (solid B) filtered. The filtrate was cooled to yield trans, cis-isomer (V), m. p. 113.5~114.5°C. This was combined with the second crop, which was obtained on diluting the filtrate A with water and recrystallized from ethanol, yielding pure trans, cis-isomer (V), in the form of colorless plates, m. p. 113.5~114.5°C, 340 mg. (32.3%). This substance showed no depression of the melting point on admixture with the specimen derived by the above-mentioned method a).

Recrystallization of the solid B from chlorobenzene yielded trans, trans-isomer I, in the form of light greenish yellow plates, m. p. 253°C, 370 mg. (35.1%). The mixed melting point determination of this substance with the specimen derived from terephthalaldehyde proved the identity.

Exposure of the mother liquor of recrystallization of trans, cis-isomer to direct sunlight resulted in a deposition of crystals. This crystals were found to

be identical with trans, trans-isomer I, m. p. 255°C, 44 mg. (4%).

The total yield of the Wittig reaction was found to be 754 mg. (71.5%).

***cis, cis-p*-Distyrylbenzene (IX).**—Two moles of hydrogen were absorbed in a period of 18 min. on the hydrogenation of a solution of *p*-bis(phenylethynyl)benzene (VIII, 80 mg.) in tetrahydrofuran (20 ml.) over Lindlar's catalyst. After removal of the catalyst, the solvent was distilled under reduced pressure, yielding crystals. Repeated recrystallization of the crystals from light petroleum afforded cis, cis-isomer IX, in the form of colorless leaflets, m. p. 86.5~87.5°C.

Found: C, 93.79; H, 6.60. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

The cost of this research was partly defrayed by the Scientific Research Expenditure Fund of the Ministry of Education, to which the authors' thanks are due.

*Department of Chemistry*
*Faculty of Science*
*Osaka University*
*Kita-ku, Osaka*

---

# *Preparation and Absorption Spectra of the Cobalt(III) Complexes of Amino Acids*[1]

By Motoshichi MORI, Muraji SHIBATA, Eishin KYUNO and Mitsuhiro KANAYA

(Received March 3, 1961)

There are two isomers, $\alpha$ (violet) and $\beta$ (red), of trisglycinatocobalt(III). It has recently been ascertained from the absorption spectra by Shimura and Tsuchida[2] and also by Basolo et al.[3] that the more soluble $\alpha$-form is a trans-cis isomer and that the other is a cis-cis isomer. This assignment is supported theoretically by Nakamoto et al.[4] Furthermore, Shimura[5] came to the same conclusion with trisalaninato cobalt(III).

The present research has two main purposes: one is an investigation on the preparation of these kinds of complexes, and the other an approach to the structures of the complexes by comparing their absorption spectra with those of model compounds having cis-cis and trans-cis structures. In addition, the thermal stability and the infrared spectra of the complexes are studied.

## Experimental

**Preparation.**—i) *Method Using Cobalt(III) Hydroxide.*—This is essentially the same as the method of Ley and Winkler[6]. To a solution of the desired amino acid was added a slight excess of freshly prepared cobalt(III) hydroxide, and the mixture was heated on a water-bath until a dark red solution was obtained. The resultant solution was filtered once to remove unreacted hydroxide. The filtrate was evaporated on a water-bath almost to dryness. The residue was dissolved in a little hot water, and the solution was filtered, if necessary. On evaporating and then standing the solution, violet crystals of the $\alpha$-form were obtained. The corresponding $\beta$-form was contaminated with the $\alpha$-form, but the amount of contamination was very small. It was very easy to purify the $\alpha$-form because of the great difference between the solubilities of the two isomers. By this method the $\alpha$-isomers of glycine, *dl*-alanine and *l*-leucine were prepared with good yields. Therefore, this method may be recommended as a general method for the $\alpha$-isomer.

Found: Co, 20.7; N, 14.8. Calcd. for $\alpha$-[Co(gly)$_3$*]: Co, 20.9; N, 14.9%. Found: Co, 18.1; N, 12.8. Calcd. for $\alpha$-[Co(ala*)$_3$]: Co, 18.2; N, 13.0%. Found: Co, 11.8; N, 18.4. Calcd. for $\alpha$-[Co(leu*)$_3$]: Co, 12.8; N, 18.6%.

ii) *Method Using Hexamminecobalt(III) Chloride.*—This method was devised by us though a similar method was reported almost at the same time[7]; the principle is based on the following equation;

$$[Co(NH_3)_6]Cl_3 + 3NH_2CH_2COOH + 3KOH \rightarrow [Co(gly)_3] + 3KCl + 3H_2O + 6NH_3$$

A mixed solution of the desired amino acid with the hexamminecobalt(III) chloride was introduced

1) Part V: On the syntheses of metal complexes. Part IV. M. Mori, M. Shibata, E. Kyuno and Y. Okubo, This Bulletin, 31, 940 (1958). Partly presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

2) Y. Shimura and R. Tsuchida, This Bulletin, 29, 311 (1956).

3) F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, 9, 810 (1955).

4) K. Nakamoto, J. Fujita, M. Kobayashi and R. Tsuchida, *J. Chem. Phys.*, 27, 439 (1957).

5) Y. Shimura, This Bulletin, 31, 173 (1958).

6) H. Ley and H. Winkler, *Ber.*, 42, 3894 (1909).

* The following abbreviations are used:
gly, $NH_2CH_2COO^-$; ala, $NH_2CH(CH_3)COO^-$;
leu, $(CH_3)_2CHCH_2CH(NH_2)COO^-$.

7) R. G. Neville and G. Gorin, *J. Am. Chem. Soc.*, 78, 4895 (1956).

into a round flask with an air condenser, and a slight excess of 3 N potassium hydroxide was added to the mixture. The whole was heated until some crystalline materials appeared in it (it took more than 1 hr.). On cooling the contents by holding the flask in running water, fine violet crystals of the $\beta$-form separated out. In this step the $\alpha$-form was not obtained even in traces, but it was produced with a poor yield on evaporating the mother liquor.

From the experiments with glycine, *dl*-alanine and *l*-leucine, it was found that this method was convenient for the preparation of the less soluble $\beta$-form.

Found: Co, 19.6; N, 13.8. Calcd. for $\beta$-[Co $(gly)_3$]: Co, 19.7; N, 14.0%. Found; Co, 18.5; N, 12.9. Calcd. for $\beta$-[$Co(ala)_3$]: Co, 18.2; N, 13.0%. Found: Co, 12.4; N, 8.8%; Calcd. for $\beta$-[$Co(leu)_3$]: Co, 12.6; N, 9.0%.

iii) *Method Using Potassium Tricarbonatocobaltate (III).*—The reaction to this method, which was also devised by us, is as follows:

$$K_3[Co(CO_3)_3]+3NH_2CH_2COOH+3CH_3COOH \rightarrow [Co(gly)_3]+3CH_3COOK+3H_2O+3CO_2$$

A desired amino acid was poured into a green solution of tricarbonatocobaltate(III) prepared by the method described in a previous paper[8], and the mixture was warmed on a water-bath for a little while, whereupon the color of the solution changed from green to blue. Then, 6 N acetic acid was added dropwise until the evolution of carbon dioxide ceased and the color of the solution became red-viotet. After filtering the solution, the filtrate was allowed to stand for some time in the cold. Crystals of the less soluble $\beta$-form were deposited, and then the $\alpha$-form separated out on evaporating the mother liquor over sulfuric acid. This method was applied to the same materials as those in i) and ii), and $\alpha$ and $\beta$ isomers were obtained in about equal amounts.

iv) *Ammoniatriacetatoethylenediaminecobalt(III),* [*Co en(ata*)*]·$H_2O$.—About 3 g. of the $\alpha$-K[Co(ata) $(OH)(OH_2)]\cdot 2H_2O$ prepared by the method described in the previous paper[9] was suspended in 20 ml. of water, and 6 ml. of a 10% solution of ethylenediamine was added to the suspension. The mixture was warmed on a water-bath until a red-violet solution was obtained. On evaporating the resultant solution over sulfuric acid, dark violet crystals of the desired complex separated out gradually. Yield, about 3 g.

Found: Co, 17.8; N, 12.7. Calcd. for [Co en (ata)]·$H_2O$: Co, 18.1; N, 12.9%.

v) *Citratotriamminecobalt(III),* [*$Co(NH_3)_3cit$***]·$H_2O$.—About 5 g. of *cis-cis*-[$Co(NH_3)_3(NO_3)_3$] and 2 g. of potassium citrate were dissolved separately in a little hot water, and the solutions were mixed and warmed on a water-bath for a few minutes. Then, about three volumes of ethanol was added to the solution, whereupon a violet oily material went to the bottom. After removal of the material by a separating funnel, the solution was kept in a refrigerator until fine rosy crystals separated out. This was slightly hygroscopic. Yield, about 1.5 g.

Found: Co, 17.9; N, 12.7. Calcd. for [Co $(NH_3)_3cit]\cdot H_2O$: Co, 18.6; N, 13.1%.

Of all the complexes prepared here, the ammoniatriacetatoethylenediamine- and the citratotriamminecobalt(III) are to be regarded as new complexes. The aqueous solutions of all the complexes are very stable against acids and heat. Their solubilities in water decrease in the order of the glycinato-, the alaninato- and the leucinato-complexes; while the leucinato-complex is soluble to a certain extent in ethanol, the glycinato-complex is sparingly soluble in it.

**Thermal Decomposition and Absorption Spectra.**—The thermal decomposition was performed by using a Shimadzu thermal-balance in the same manner as that described in a previous paper[9]. The absorption spectra in solution were measured by a Hitachi EPU spectrophotometer, and the infrared spectra were obtained with a Koken DS 201 infrared spectrophotometer equipped with sodium chloride optics.

## Results and Discussion

**Thermal Decomposition.**—The decomposition curves of the glycinato-, alaninato- and leucinato-complexes are shown in Figs. 1—2 in which the weight loss per formual weight was plotted against temperature. In the case of the $\beta$-glycinato-complex, there is a certain weight loss corresponding to one molecule of water at 100~150°C, but there is no such weight loss in the corresponding $\alpha$-complex. It has been believed that the $\alpha$-complex has two molecules of water of crystallization, but the compound obtained in the present study is anhydrous. The decompositions of both isomers begin at nearly 220°C, and the weight loss corresponding to three molecules of

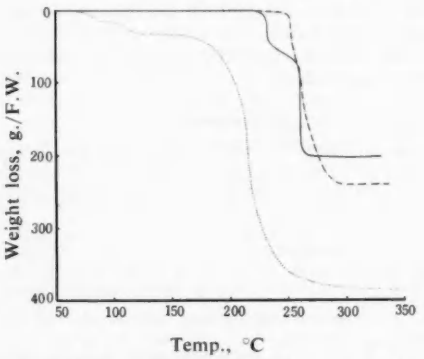



Fig. 1. Thermal decomposition curves of:
—— $\alpha$-[$Co(gly)_3$]
-·-· $\alpha$-[$Co(ala)_3$]
····· $\alpha$-[$Co(leu)_3]\cdot 2H_2O$

8) M. Mori, M. Shibata, E. Kyuno and T. Adachi, This Bulletin, 29, 883 (1956).

* Abbreviation ata stands for ammoniatriacetate ion.

9) M. Mori, M. Shibata, E. Kyuno and Y. Okubo, This Bulletin, 31, 940 (1958).

* Abbreviation cit stands for citrate ion.

ammonia is clearly observed at the first stage of decomposition. In the cases of the $\alpha$- and the $\beta$-alaninato-complex there is no evidence for the existence of water of crystallization and the decomposition temperatures are about 250°C. For the $\alpha$-isomer of the leucinato-complexes, the removal of water takes place in two steps and the total amounts correspond to $2H_2O$. On the other hand, the $\beta$-isomer may be anhydrous because no distinct weight loss is observed. The decomposition temperatures are in the neighborhood of 180°C. In general, it may be said that the $\alpha$-forms are less stable than the corresponding $\beta$-forms, though the difference in the decomposition temperature is not very large.

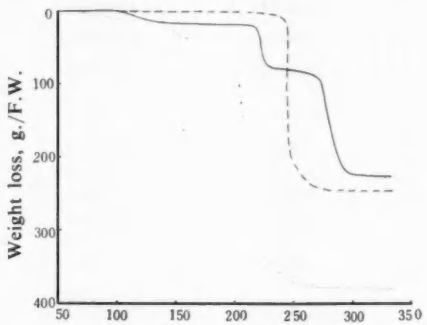



Fig. 2. Thermal decomposition curves of:
—— $\beta$-$[Co(gly)_3]\cdot H_2O$
-·-· $\beta$-$[Co(ala)_3]$
····· $\beta$-$[Co(leu)_3]$

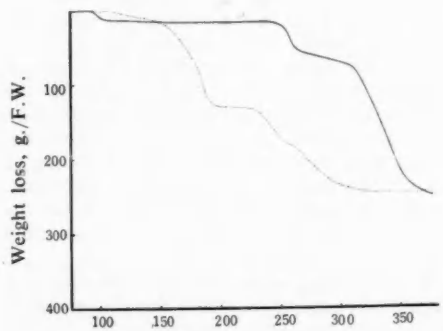



Fig. 3. Thermal decomposition curves of:
—— $[Co\ en(ata)]\cdot H_2O$
····· $[Co(NH_3)_3cit]\cdot H_2O$

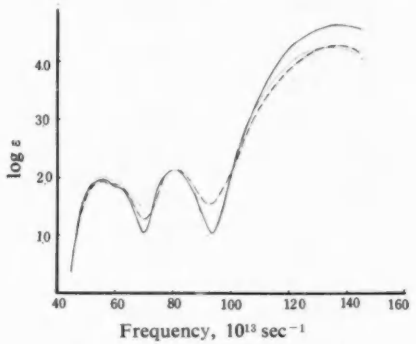



Fig. 4. Absorption spectra of:
—— $\alpha$-$[Co(gly)_3]$
-·-· $\alpha$-$[Co(ala)_3]$
····· $\alpha$-$[Co(leu)_3]\cdot H_2O$

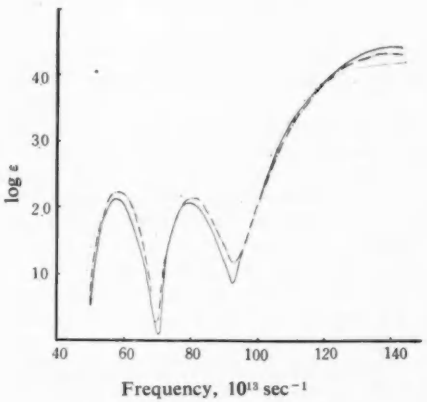



Fig. 5. Absorption spectra of:
—— $\beta$-$[Co(gly)_3]$
-·-· $\beta$-$[Co(ala)_3]$
····· $\beta$-$[Co(leu)_3]\cdot H_2O$

TABLE I. ABSORPTION MAXIMA AND log $\varepsilon$ ($10^{13}$/sec.)

| | $\nu_1$ | log $\varepsilon_1$ | $\nu_2$ | log $\varepsilon_2$ | $\nu_3$ | log $\varepsilon_3$ | $\nu_2$ calcd | $\Delta$ |
|---|---|---|---|---|---|---|---|---|
| $\alpha$-$[Co(gly)_3]$ | 55.4 | 1.97 | 80.4 | 2.15 | 136.4 | 4.64 | 79.18 | +1.22 |
| $\alpha$-$[Co(ala)_3]$ | 55.6 | 1.96 | 80.7 | 2.16 | 135.8 | 4.34 | 79.42 | +1.28 |
| $\alpha$-$[Co(leu)_3]\cdot 2H_2O$ | 55.6 | 2.04 | 80.0 | 2.23 | 135.8 | 4.30 | 79.42 | +0.58 |
| $[Co\ en(ata)]\cdot H_2O$ | 57.5 | 2.20 | 82.0 | 2.24 | 133.9 | 4.59 | 81.68 | +0.32 |
| $\beta$-$[Co(gly)_3]\cdot H_2O$ | 57.7 | 2.16 | 79.6 | 2.08 | 140.2 | 4.45 | 81.92 | −2.32 |
| $\beta$-$[Co(ala)_3]$ | 58.0 | 2.22 | 80.4 | 2.21 | — | — | 82.27 | −1.87 |
| $\beta$-$[Co(leu)_3]\cdot H_2O$ | 58.0 | 2.27 | 80.4 | 2.26 | — | — | 82.27 | −1.87 |
| $[Co(NH_3)_3cit]\cdot H_2O$ | 56.4 | 1.58 | 79.8 | 1.92 | — | — | 80.37 | −0.57 |

TABLE II. INFRARED ABSORPTION

| Assignment | | α-[Co(gly)$_3$] | β-[Co(gly)$_3$] | α-[Co(ala)$_3$] | β-[Co(ala)$_3$] |
|---|---|---|---|---|---|
| | | | 3356(sh) | 3460(w) | |
| st | $NH_2$ | 3106(sh) | 3106(sh) | 3125(s) | 3096(sh) |
| | | | 1621(vs) | | 1634(vs) |
| st-a | $CO_2$ | 1618(vs) | 1585(vs) | 1629(vs) | 1582(vs) |
| st-s | $CO_2$ | 1351(sh) | 1350(sh) | 1344(sh) | 1344(sh) |
| d, w | $NH_2$ | 1299(m) | 1302(s) | 1282(s) | 1274(vs) |
| st-a | CCN | 1233(m) | 1205(s) | 1238(w) | 1250(w) |
| d, t | $CH_2$ | 1181(s) | 1174(s) | 1190(m) | 1190(m) |
| d, t | $NH_2$ | 1036(w) | 1030(w) | 1024(w) | 1028(w) |
| d, r | $CH_2$ or $NH_2$ | 955(w) | 963(m) | — | — |
| st-s | CCN | 911(m) | 919(m) | 924(m) | 923(m) |
| | | | | 864(s) | 858(s) |
| d, r | $NH_2$ | 819(m) | 821(m) | 821(w) | 821(sh) |
| or d, r | $CH_2$ | 778(w) | 776(m) | 806(w) | 807(m) |
| | | | 759(w) | | |
| d | $CO_2$ | 753(m) | 755(w) | 763(w) | 761(w) |
| | | | | | 1124(sh) |
| | ? | 1133(s) | 1149(s) | 1126(s) | 1109(m) |

* K. Nakamura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 80, 113 (1959). The abbreviations used in the first column of the table of assignments are: st, bond stretching vibration; d, deformation vibration; r, rocking vibration; w, wagging vibration; t, twisting vibration; ?, assignment uncertain; -s, symmetric vibration; -a, asymmetric vibra-

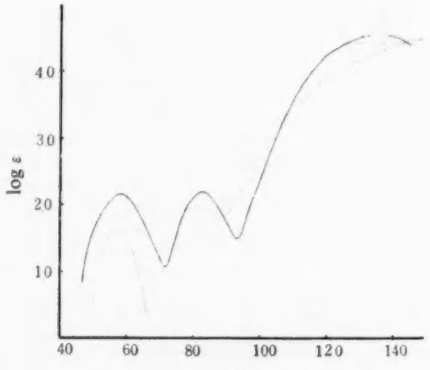



Fig. 6. Absorption spectra of:
—— [Co en(ata)]·$H_2O$
····· [$Co(NH_3)_3$cit]·$H_2O$

The decomosition curves for the ammoniatriacetato- and the citrato-complex are shown in Fig. 3. The former complex loses one molecule of water at a temperature below 100°C and begins to decompose at about 240°C. The latter is dehydrated at about 150°C and then decomposed when the temperature is raised.

**Visible and Ultraviolet Absorption Spectra.**— The absorption spectra of the α- and the β-forms are summarized in Figs. 4 and 5 respectively. The characteristic difference between them is seen in the first and the third bands; all of the first bands of the α-forms are more or less splitted, while those of the β-forms are normal and sharp. The third bands for the α-forms are sharper than those for the β-forms.

The absorption curves of the ammoniatriacetato- and the citrato-complex are shown in Fig. 6. The former complex has a somewhat split first band and a distinct third band, but the latter has a sharp first band and no maximum in the region of the third band.

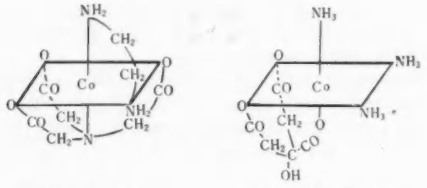
As mentioned above, the ammoniatriacetato-complex is taken as a model for the trans-cis configuration and the citrato-complex for the cis-cis configuration, because ammoniatriacetate ion acts as a tetradentate donor and citrate ion is a tridentate ligand; consequently the most probable structures of the two complexes are thought to be those given in Fig. 7. From the similarity of the absorption spectra, it may be concluded that all the α-forms have the trans-cis structure and the β-forms, the cis-cis. The same conclusion has been reached by others[2,3,5] but a somewhat different approach was adopted in our study.

The numerical data of the absorption spectra of these complexes are summarized in Table I; the absorption maxima for the second bands reveal a general relationship between the α- and β-isomers. In the last two columns of

BANDS($cm^{-1}$) FOR AMINOACIDS COMPLEXES

| α-[Co(leu)$_3$] | β-[Co(leu)$_3$] | [Co en(ata)]·$H_2O$ | [Co$(NH_3)_3$cit]·$H_2O$ | $NH_2$-$CH_2$-COOH* |
|---|---|---|---|---|
| | | 3413(w) | 3425(sh) | |
| 3175(sh) | 3175(sh) | 3145(m) | 3175(sh) | |
| | 1639(vs) | | | |
| 1634(vs) | 1613(vs) | 1631(vs) | 1577(vs) | 1572(vs) |
| 1325(sh) | 1333(s) | 1323(m) | 1328(s) | 1412(s) |
| 1299(m) | 1299(m) | 1266(m) | 1271(m) | 1133(m) |
| | | | | 1109(m) |
| 1235(w) | 1266(w) | 1229(w) | 1232(s) | 1034(s) |
| 1160(m) | 1190(w) | 1198(w) | 1170(w) | |
| 1073(w) | 1040(w) | 1059(m) | 1067(s) | |
| 988(w) | 971(w) | 957(w) | 938(w) | 909(sh) |
| 926(w) | 924(w) | 913(s) | 914(w) | 892(s) |
| 847(m) | 843(m) | 849(sh) | 862(s) | |
| 821(w) | 820(w) | | 820(sh) | |
| 794(w) | 777(w) | | | |
| 758(w) | 727(s) | 758(s) | 727(s) | 696(s) |
| 1127(w) | 1134(w) | 1152(s) | 1140(s) | |

tion. The abbreviation used in the body of the table of assignments to indicate the relative intensities of the absorption are; vs, very strong; s, strong; m, medium strong; w, weak; sh, shoulder.




[Co en(ata)] [Co$(NH_3)_3$cit]

Fig. 7. Probable structures.

the table, the values calculated by a Sone's equation[10] and the differences ($\Delta$) of the calculated values from the observed maxima are given. All of the trans-cis isomers show positive difference and the cis-cis isomers, negative difference.

**Infrared Spectra.**—The numerical data of the infrared spectra are summarized in Table II, in which the assignment is carried out with reference to papers of Nakamura and others[11]. A distinctive difference between the absorption of α- and β-isomers is observed in the region of 1580~1630 $cm^{-1}$; there is only one peak for the α-isomer, but the β-isomer has two split absorption peaks. Among the isomers of the same type, the absorption maxima shifted to longer wavelengths in the following order: the leucinato-, the alaninato- and the glycinato-complexes.

**Preparation.**—It is very interesting that the methods mentioned in the Experimental section above have preferential properties for the production of cis-cis and trans-cis isomers; the cobalt(III) hydroxide method favors the trans-cis, the hexammine method is advantageous for the cis-cis, and the tricarbonato method gives both isomers in the about the same amount. Therefore, somewhat different mechanisms may be involved in these methods and perhaps in the formation of the isomers; the decisive factor is which of the nitrogen and oxygen atoms of the incoming donor attacks the objects first.

## Summary

Three different methods were investigated of the preparation of trisglycinato-, trisalaninato- and trisleucinato-cobalt(III). The method using cobalt(III) hydroxide is convenient for the α-form, the method using hexamminecobalt(III) salt is advantageous for the β-form, and the method using tricarbonatocobaltate(III) gives both forms of the complexes. In addition, two new isomers of [Co en(ata)]·$H_2O$ and [Co$(NH_3)_3$cit]·$H_2O$ having trans-cis and cis-cis

10) K. Sone, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **71**, 270 (1950).
11) K. Nakamura, ibid., **80**, 113 (1959); S. Mizushima and I. Nakagawa, ibid., **80**, 124 (1959).

configurations with respect to the coordinated atoms were synthesized.

By comparing the visible and the ultraviolet absorption spectra, it was concluded that the $\alpha$-form is a trans-cis isomer and that the $\beta$-form is a cis-cis isomer. Thermal decomposition of the complexes was performed in order to estimate the water of crystallization and the stability. The infrared spectra of the complexes were also measured.

*Department of Chemistry*
*Faculty of Science*
*Kanazawa University*
*Kanazawa*

# *Studies on Metal Complex Species Using an Anion Exchange Resin. II. On the Adsorption of Silver from Nitrate Solution*

By Hirohiko WAKI

(Received January 16, 1961)

In the previous papers[1,2] the author has derived equations for determining the composition of a metal complex by use of an anion exchange resin and applied them to mercury(II)-nitrate complex species. Silver is, as well as mercury, adsorbed on an anion exchange resin from solutions of various nitrates or nitric acid, though its adsorption is not strong. In this paper the adsorption of silver from nitrate solutions and nitric acid was studied and its form in the resin was determined by the previously reported method[1,2] as well as by a new method.

The adsorption of silver nitrate on an anion exchanger Dowex 1-X8 was examined and compared with that of alkali nitrates. Even alkali nitrates are taken up a little in the resin, but no appreciable difference in the adsorbability between sodium and potassium is evident, as shown in Fig. 1. The apparent adsorption of alkali metals may be considered merely as a permeation of dissociated normal salts. On the other hand, the adsorbed amount of silver nitrate is considerably larger than that of alkali nitrates.

This difference in the adsorbability between silver and alkali metals is remarkable when a small quantity of these elements is used in a nitric acid medium, as shown in Fig. 2. The

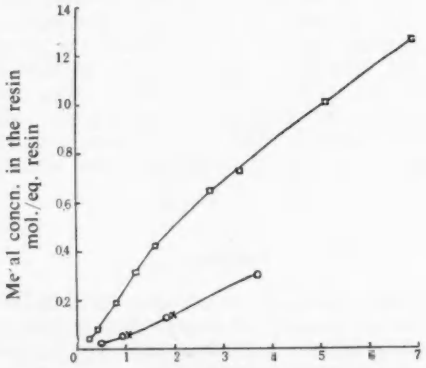



Fig. 1. Adsorption of Ag, Na and K from the solution of its nitrate only.
□ $AgNO_3$ ○ $NaNO_3$ × $KNO_3$

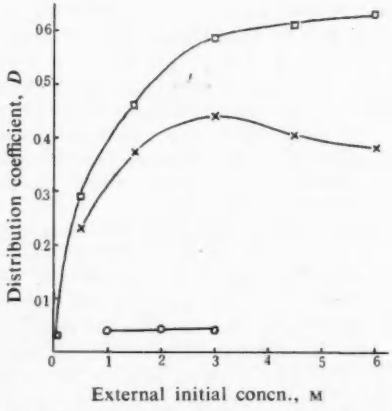



Fig. 2. Adsorption of Ag and Na in small quantity from nitrate solutions.
Metal: 0.1 mmol., Resin: 3 g., Solution: 8 ml.
□ Ag in $NaNO_3$ × Ag in $HNO_3$
○ Na in $HNO_3$

1) H. Waki, This Bulletin, 33, 1469 (1960).
2) H. Waki, ibid., 34, 829 (1961).

distribution coefficient of sodium is very small and scarcely increases at all with an increase in nitric acid concentration. On the other hand, the distribution coefficient of silver in nitric acid increases rapidly in the beginning, then gradually to a maximum near 3 M nitric acid and then decreases gradually. In sodium nitrate solution, the coefficient has no maximum and is somewhat greater than that in nitric acid. Although the coefficient is considerably smaller than that of mercury[1,2], it may be reasonable to consider that the adsorption of silver is not a simple permeation of the normal salt but is related to the formation of nitrate complex species.

However, silver ion does not appear to form any nitrate complex anion in an ordinary nitrate solution, since silver nitrate may be regarded as a kind of relatively strong electrolyte, as seen from the fact that the mean activity coefficient[3] of silver nitrate is similar to that of alkali nitrate, especially that of potassium nitrate and rubidium nitrate, and at the utmost the presence of undissociated silver nitrate[4] may be considered only in concentrated nitrate solution. Even if a slight quantity of the complex anion is present in the solution, it may be difficult to consider that the adsorption of silver takes place by a successive permeation of the complex, because it takes only a short time to reach the adsorption equilibrium. Accordingly, the adsorption of silver may be explained by its movement into the resin phase as silver ion $Ag^+$ and neutral species $AgNO_3^0$, followed by the conversion into a silver-nitrate complex in the resin phase.

For the purpose of determining the composition of a metal complex by use of an anion exchange resin, the distribution coefficient $D$ of a metal element was expressed as follows[1,2]:

$$\log D=\left(n-\frac{a}{b}\right)\log[X^{b-}]-\left(m-\frac{a}{b}\right)\log(X^{b-})+K+G \qquad (1)$$

where ( ) and [ ] indicate the concentrations in the solution phase and the resin phase, $m$ and $n$ represent the numbers of an anion $X^{b-}$ binding to one metal ion $M^{a+}$ in these phases, and $K$ and $G$ represent the terms containing the complex formation constants and the activity coefficients in both phases, respectively. When the metal is present as $M^{a+}$ in the solution, Eq. 1 may be written as follows:

$$\log D=\left(n-\frac{a}{b}\right)\log[X^{b-}]+\frac{a}{b}\log(X^{b-})+K+G \qquad (2)$$

if a similar assumption is made in a silver-nitrate system, the following equation is obtained.

$$\log D-\log(NO_3^-)=(n-1)\log[NO_3^-]+K+G \qquad (3)$$

**Experiment by the Addition of an Indifferent Anion.**—This experiment was carried out in a way similar to that in the mercury-nitrate system. Two grams of an anion exchanger Dowex 1-X8 (100~200 mesh) of nitrate form was mixed with 10 ml. of a solution containing 0.3 mmol. of silver nitrate and a series of mixtures of sodium nitrate and sodium perchlorate of various mixing ratios (total concentration is 3 M). After equilibrium is reached silver and nitrate in the resin were determined. Silver was analyzed titrimetrically with a potassium thiocyanate and nitrate spectrophotometrically at 300 mμ. The amounts of silver and nitrate in the solution were estimated by subtraction from their total amounts.

The ion concentrations in the resin phase were always represented as millimoles of the ion per milliequivalent of the resin. The distribution coefficient of silver was calculated as

$$D=\frac{\text{mmol. of Ag adsorbed per meq. of the resin}}{\text{mmol. of Ag per ml. of the soln.}}$$

After the nitrate concentration in the resin was corrected as in the case of mercury-nitrate, $\log D-\log(NO_3^-)$ was plotted against the logarithm of the nitrate ion concentration in the resin. As shown in Fig. 3, in the range where nitrate is predominant, the gradient of the curve is 0.9, which corresponds approximately to $n=2$. From this result, it may be recognized that most of the silver-nitrate complex adsorbed from 3 M sodium nitrate solution has the form of $Ag(NO_3)_2^-$.

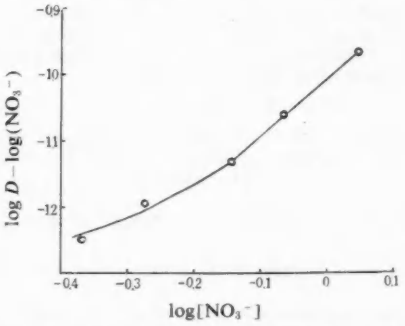



Fig. 3. Distribution coefficient of Ag as a function of the nitrate concentration in the resin phase. The measurements were carried out at the nitrate-rich range. Total concentration of the external solution is 3 M.

3) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths Scientific Publications, London (1955).
4) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part II Inorganic Ligands", London (1958).

TABLE I. EQUILIBRIUM DATA ON THE BATCH EXPERIMENT

A. 2 M Series — Resin : 7.14 meq., Solution : 8 ml.

| Batch No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $AgNO_3$ given, mmol. | 0.100 | 1.275 | 1.985 | 3.97 | 5.96 | 7.94 | 11.91 |
| $NaNO_3$ given, mmol. | 16.00 | 14.72 | 14.00 | 12.00 | 10.00 | 8.00 | 4.00 |
| (Ag)mmol./ml. | 0.00813 | 0.112 | 0.175 | 0.361 | 0.559 | 0.755 | 1.175 |
| [Ag]mmol./meq. | 0.00490 | 0.0536 | 0.0819 | 0.152 | 0.209 | 0.266 | 0.352 |
| $D$ ml./meq. | 0.603 | 0.481 | 0.468 | 0.420 | 0.373 | 0.352 | 0.299 |
| $(NO_3^-)$mmol./ml. | 1.88 | 1.83 | 1.80 | 1.76 | 1.73 | 1.66 | 1.59 |
| $[NO_3]_t$ mmol./meq. | 1.15 | 1.19 | 1.22 | 1.27 | 1.30 | 1.37 | 1.45 |
| $\log D - \log(NO_3^-)$ | −0.494 | −0.581 | −0.585 | −0.622 | −0.666 | −0.673 | −0.726 |

B. 3 M Series — Resin : 6.45 meq., Solution : 8 ml.

| Batch No. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $AgNO_3$ given, mmol. | 0.100 | 0.985 | 1.97 | 3.94 | 5.91 | 7.88 |
| $NaNO_3$ given, mmol. | 24.07 | 23.07 | 22.06 | 20.06 | 18.05 | 16.04 |
| (Ag)mmol./ml. | 0.00805 | 0.0838 | 0.171 | 0.349 | 0.539 | 0.733 |
| [Ag]mmol./meq. | 0.00552 | 0.0488 | 0.0938 | 0.178 | 0.247 | 0.313 |
| $D$ ml./meq. | 0.686 | 0.583 | 0.550 | 0.551 | 0.459 | 0.428 |
| $(NO_3^-)$mmol./ml. | 2.83 | 2.78 | 2.75 | 2.70 | 2.69 | 2.62 |
| $[NO_3]_t$ mmol./meq. | 1.24 | 1.28 | 1.30 | 1.37 | 1.38 | 1.46 |
| $\log D - \log(NO_3^-)$ | −0.256 | −0.343 | −0.374 | −0.428 | −0.478 | −0.533 |

**Experiment by the Loading of the Complex.**— In determining the composition of a metal complex, a method in which the ratio of the adsorbed amount of the metal to the exchange capacity of the resin is determined after the resin is saturated with the metal complex anion, has often been employed[5]. This method is simple and reliable when the complex is stable and strongly adsorbed on an anion exchanger. However, it can not be used when the complex is unstable and not strongly adsorbed.

In view of this, a new loading method was studied by the present writer, which is based on Eq. 2. In the proposed method, instead of the addition of the indifferent anion, a greater amount of the same metal element is used to keep the ionic strength in the solution phase constant. The ligand ion concentration in the resin phase is therefore varied by the loading of the metal complex instead of an indifferent anion. Assuming that $MX_n^{(bn-a)-}$ is only one species for the resin phase, this concentration is expressed by

$$[X^{b-}] = [X]_t - n[MX_n^{(bn-a)-}] \quad (4)$$

where $[X]_t$ is the total ligand concentration irrespective of species. From Eq. 2 and Eq. 4 the following equation is obtained.

$$\log D = \left(n - \frac{a}{b}\right)\log([X]_t - n[MX_n^{(bn-a)-}]) + \frac{a}{b}\log(X^{b-}) + K + G \quad (5)$$

When a considerable amount of the metal is adsorbed, for the determination of $n$, $\log D/(X^{b-})^{a/b}$ can not be plotted against $\log[X^{b-}]$, because the second term in the right side of Eq. 4 can not be neglected and $n$ is unknown. Accordingly, in this case $\log D/(X^{b-})^{a/b}$ is plotted against $[MX_n^{(bn-a)-}]$ and the slope of the curve should be compared with that of the standard curves drawn by substituting 1, 2, 3, ……for $n$ in Eq. 5.

In a system of silver nitrate and sodium nitrate, Eq. 5 is written as follows:

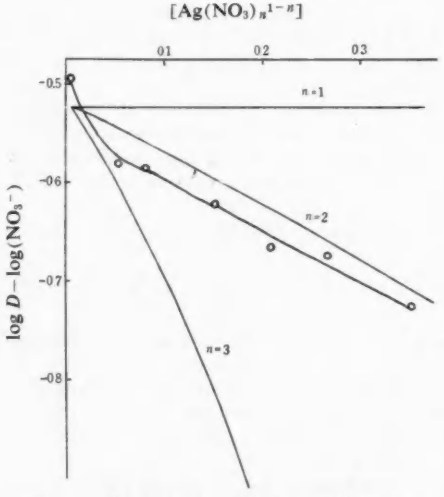



Fig. 4. Comparison with the standard curves in the system where the external initial concentration of $AgNO_3 + NaNO_3$ is 2 M.
The standard curves are drawn in a position in which their gradients may compare with that of experimental curve.
-○- Measured —— Standard

5) For example, R. A. Horne, R. H. Holm and M. D. Meyers, *J. Phys. Chem.*, **61**, 1955 (1957).

$$\log D - \log(NO_3^-) = (n-1)\log([NO_3]_t - n[Ag(NO_3)_n^{(n-1)-}]) + K + G \quad (6)$$

The experiment was carried out by equilibrating 3 g. of an anion exchanger Dowex 1-X8 (100~200 mesh) of nitrate form with 10 ml. of a solution containing a series of mixtures of silver nitrate and sodium nitrate of various mixing ratios (total concentration is 2 M or 3 M), followed by determination of silver and nitrate in the solution phase. The silver concentration in each phase and the distribution coefficient were estimated in the same way as before. The nitrate in the solution was determined by titrating with a sodium hydroxide solution, after it was converted into nitric acid through a cation exchange column of hydrogen form. The amount of total nitrate in the resin was estimated by subtraction.

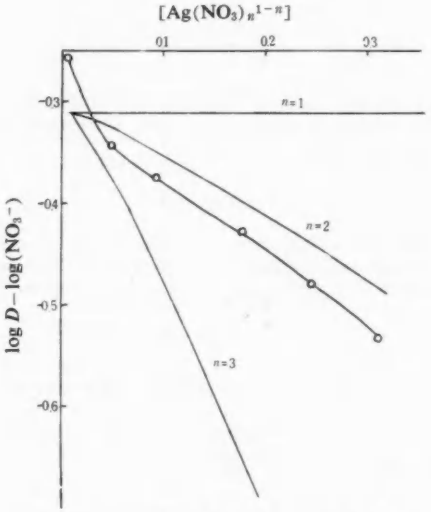



Fig. 5. Comparison with the standard curves in the system where the external initial concentration of $AgNO_3+NaNO_3$ is 3 M.
The standard curves are drawn in a position in which their gradients may compare with that of experimental curve.
-○- Measured —— Standard

The equilibrium data are tabulated in Table I and the curves for analysis are drawn in Fig. 4 and Fig. 5. Each slope of the curve is similar to that of the standard curve for $n=2$ in a wide range of the silver concentration except at a very low concentration. From this fact it may be considered that most silver in the resin phase exist as $Ag(NO_3)_2^-$ at the external nitrate concentration of about 2~3 M. This result is in agreement with that in the former experiment carried out by the addition of an indifferent anion. The high value of the gradient at the low concentration of silver is presumably due not to the presence of higher nitrate complexes, but to the inconstancy of the activity coefficient term in this region.

## Summary

1) It was found that silver was to some extent adsorbed on a strong base anion exchange resin from nitrate solutions. Its behavior was significantly different from that of alkali metals.

2) The equations derived in the previous paper were applied to a study of silver-nitrate complex. Starting from the same equation, two methods using either $NaNO_3+NaClO_4$ mixed media or the loading of the complex were employed, and the two results were in good agreement.

3) It was presumed that most silver in the resin exists as $Ag(NO_3)_2^-$ in neutral nitrate media where the external nitrate concentrations were about 2~3 M, although such anionic species may not be considered to exist in an ordinary nitrate solution.

The author wishes to express his sincere thanks to Professor Jun Yoshimura of Kyushu University for his guidance and encouragement. He also thanks Professor Hidetake Kakihana of Tokyo Technical University for his valuable suggestion.

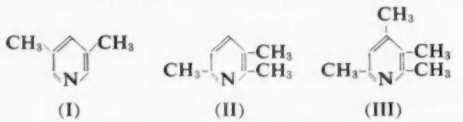
*Department of Chemistry*
*Faculty of Science*
*Kyushu University*
*Hakozaki, Fukuoka*

# *Separations of Lutidines, Collidines and 2, 3-Cyclopentenopyridines from Coal Tar Bases*

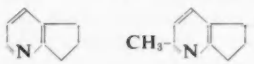
By Hajime SUZUMURA

(Received April 10, 1961)

In order to examine the tertiary amines in coal tar bases, especially in a forerunning of quinoline, methods of picrate and urea adduct formation, countercurrent extraction and chromatography were applied in order to effect the isolation of the bases. Selective separations could be carried out easily for some of the high boiling bases. From a fraction boiling at 170°C, 3, 5-lutidine[1] (I) was separated relatively easily as a zinc chloride adduct, and 2, 3-disubstituted pyridines such as 2, 3, 6-collidine[1] (II), 2, 3, 4, 6-tetramethylpyridine[2,3] (III), 2, 3-cyclopentenopyridine[2] (IV) and 2, 3-cyclopenteno-6-methylpyridine[3-5] (V) were isolated as

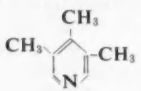


(I) (II) (III)



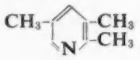
(IV) (V)

urea adducts from the fractions with corresponding boiling points. Furthermore, using a chromatographic column of cupric chloride-aluminum oxide which was effective for separations of pyridine, picolines and lutidines[6,7]



(VI)

2, 3-cyclopenteno-6-methylpyridine and 3, 4, 5-collidine[4,8-10] (VI) were separated. The latter was isolated for the first time from coal tar bases by the author[8]. With the same chromatographic column, 2, 3, 5-collidine[10] (VII) could also be separated and purified.



(VII)

The properties and physical constants of the bases which were separated are shown in the following tables.

## Experimental

**Materials.**—The materials used in the present investigation were all supplied by Yawata Chemical Industry Co.; their properties are shown below.

TABLE I. 3,5-LUTIDINE

| | B. p. °C | $d_4^{25}$ | M. p. of $B(HgCl_2)_2HCl$ °C | M. p. of picrate °C |
|---|---|---|---|---|
| Isolated | 171~172 | 0.9390 | 169~170 | 244~244.5 |
| Reported[1] | 171 | 0.9385 | 170 | 240 |

TABLE II. 2,3,6-COLLIDINE

| | B. p. °C | M. p. of picrate °C | $n_D^{25}$ |
|---|---|---|---|
| Isolated | 171~171.5 (uncorr.) | 147.4~148.4 | 1.5020 |
| Reported[1] | 172.8 | 148 | |

TABLE III. 2,3,4,6-TETRAMETHYLPYRIDINE

| | B. p. °C | $n_D^{25}$ | N % | M. p. of picrate °C | M. p. of picrolonate °C | Ultraviolet spectrum in cyclohexane $\lambda_{max}$ mμ | $\varepsilon_{max}$ |
|---|---|---|---|---|---|---|---|
| Isolated | 202.5 | 1.5088 | 10.35 | 122~122.5 | 226.4~226.9 | 266 | 3294 |
| Reported[2] | 203.3 | 1.5087 | (10.37)* | 122.5~123 | 225.5 | 266.5 | 3210 |

* Calcd.

1) T. Eguchi, This Bulletin, 3, 227 (1928).
2) P. Arnall, *J. Chem. Soc.*, 1954, 4040.
3) S. Jifuku, S. Nakayama, H. Suzumura and M. Uemura, *J. Japan Tar Ind. Association*, 10, 126 (1958).
4) P. Arnall, *J. Chem. Soc.*, 1958, 1202.
5) S. Tanaka et al., *Japan Analyst* (*Bunseki Kagaku*), 6, 281 (1957).
6) R. Vignes et al., *Compt. rend.*, 232, 1419 (1951).
7) E. Funakubo, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 59, 220 (1956).
8) Annual Meeting of Japan Tar Industry Association, October, 1956.
9) A. S. Bailey et al., *J. Chem. Soc.*, 1959, 2554.
10) K. Tsuda et al., *Pharm. Bull.*, 1, 283 (1953).

Table IV. 2,3-Cyclopentenopyridine

| | B. p. °C | $n_D^{25}$ | M. p. of picrate °C | M. p. of picrolonate °C | Ultraviolet spectrum $\lambda_{max}$ mμ | $\varepsilon_{max}$ |
|---|---|---|---|---|---|---|
| Isolated | 199.5 | 1.538 | 183.5~184 | 238.8 | 272 | 4090 |
| Reported[2] | 199.3~199.4 | 1.541 | 182~183 | 239 | | |

Table V. 2,3-Cyclopenteno-6-methylpyridine

| | B. p. °C | F. p. °C | $n_D$ | M. p. of picrate °C | M. p. of picrolonate °C |
|---|---|---|---|---|---|
| Isolated | 210.5~211 | 35.0~35.7 | 1.527 (40°C) | 152.1~152.6 | 205.5~206.5 |
| Reported[4] | 211.9(761mmHg) | 31.8 | 1.5297(32.5°C) | 155 | 170 |
| Reported[5] | | 35·0 | | 152.8~153.1 | |

Table VI. 3,4,5-Collidine

| | B. p. °C | M. p. °C | $d_4^t$ | $n_D$ | M. p. of picrate °C | M. p. of picrolonate °C | N % |
|---|---|---|---|---|---|---|---|
| Isolated | 210.3~210.8 | 32.6~35.6 | 0.955 (35°C) | 1.5115 (35°C) | 173.6~174.3 | 224 | 11.25 |
| Reported[4] | 211.4~211.5 (759 mmHg) | 36.8 | 0.947 (40°/20°C) | 1.5132 (37°C) | 178 | 232 | |
| Reported[9] | — | — | — | — | 174~175 | 228 | |
| Reported[10] | 205~207 | 10~13 | 0.9616 (15°C) | 1.5103 (15°C) | 174 | 188 | Calcd. 11.52 |

Table VII. 2,3,5-Collidine

| | B. p. °C | $n_D^{25}$ | M. p. of chloroplatinate °C | M. p. of picrate °C |
|---|---|---|---|---|
| Isolated | 185~185.8 | 1.5045 | 211 | 184.5~185.2 |
| Reported[10] | 186.8 | 1.5057 | 212 | 184 |

Table VIII

Forerunning of quinoline ($S_1$)

Toluidine fraction
b. p. 199.8~202.2°C (28%)
↓
Tertiary amines (21%) ($T_3$)
↓ distilled
b. p. 183~189°C 32%
b. p. 200~201°C 17%

Xylidine fraction
b. p. 210.5~225°C (12%)
↓
Tertiary amines (50%) ($X_3$)
↓ distilled (30 mmHg)

| No. of fraction | Temp. of distillation °C | Yield* % |
|---|---|---|
| 2 | 95~ 96 | 8.8 |
| 3 | 96~100.5 | 13.2 |
| 4 | ~102 | 11.0 |
| 5 | ~104 | 8.0 |
| 6 | ~105 | 14.6 |
| 7 | ~108 | 17.2 |
| 8 | 108 | 13.0 |

* The yield in each step is based on an immediately preceding material.

Table IX. 2,3-Cyclopenteno-6-methylpyridine

| No. of fraction | Urea adduct Amount g. | Urea adduct M. p. °C | Base recovered from urea adduct g. | Picrate Amount g. | Picrate M. p. °C |
|---|---|---|---|---|---|
| 7 | — | 86~129 | 1.4 | 0.35 | 149~150.5 |
| 8 | 2.4 | 88~129 | 1.3 | 0.80 | 150~150.5 |
| 9 | 2.6 | 88~129 | 1.3 | 0.90 | 150~150.5 |

TABLE X. 3,4,5-COLLIDINE AND 2,3-CYCLOPENTENO-6-METHYLPYRIDINE

| No. of band | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Base recovered from each band, g. | 0.25 | 0.25 | 0.39 | 2.6 | 2.4 | 1.9 | 0.8 |
| M. p. of picrate, °C | 170.5~172.5 | 171~172 | | 150~151 | 150~151 | 192~195 | |
| Amount of picrate, g. | 0.7375 | 0.6425 | | 3.0 | 1.4 | 0.4 | |
| Compound | 3,4,5-Collidine | | | 2,3-Cyclopenteno-6-methylpyridine | | Unidentified | |

TABLE XI.

| No. of fraction | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Amount, g. | 8.4 | 5.0 | 3.4 | 5.4 |
| $n_D^{25}$ | 1.5093 | 1.5094 | 1.5115 | 1.5201 |
| M. p.* of picrate, °C | 124~138 | 113~125 | 124~150 | 178~179 |

* After recrystallized twice from ethanol.

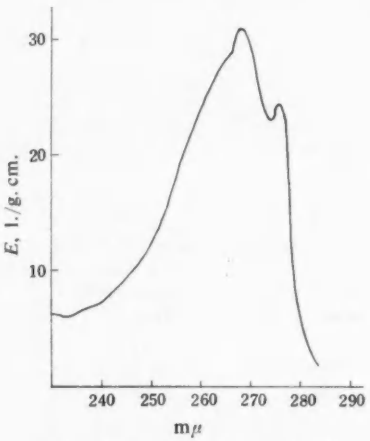



Fig. 1. 3,5-Lutidine in ethanol.

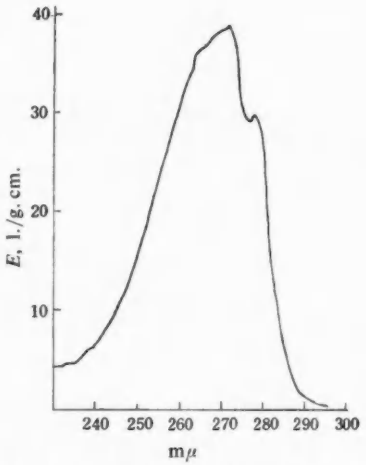



Fig. 3. 2,3-Cyclopentenopyridine.

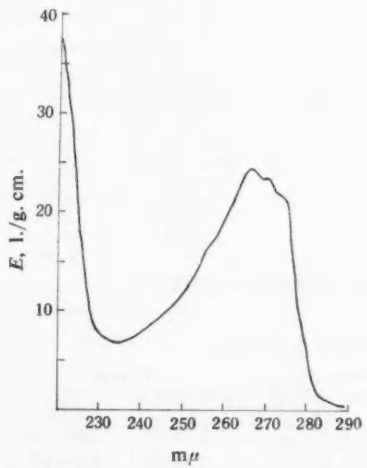



Fig. 2. 2,3,4,6-Tetramethylpyridine.

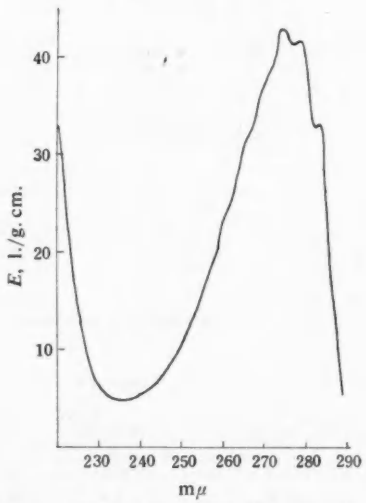



Fig. 4. 2,3-Cyclopenteno-6-methylpyridine.

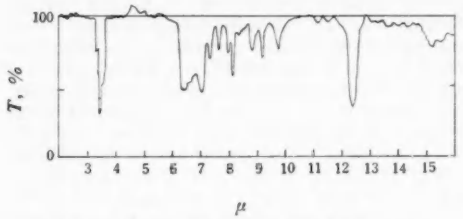



Fig. 5. 2,3-Cyclopenteno-6-methylpyridine.

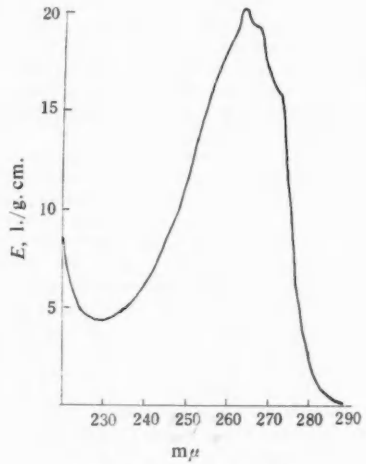



Fig. 6. 3,4,5-Collidine.

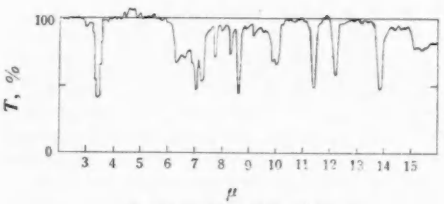



Fig. 7. 3,4,5-Collidine.

(1) Industrial grade collidine grade 1

| Sample | First drop | 10% | 50% | 90% | Dry point |
|---|---|---|---|---|---|
| A | 165.7 | 171.7 | 173 | 178 | 180 |
| B | 161.0 | 166.0 | 172 | 181 | 185 |

(2) Tertiary amines boiling at 200 and 210°C. A forerunning of quinoline (Fig. 8) was obtained when the crude quinoline was first extracted with sulfuric acid from the middle oil of coal tars and then fractionally distilled. Fractionating through a packed column 3 m. in height, this forerunning was separated into toluidine and xylidine fractions. Primary amines in these fractions were removed by acetylation, and the mixture of tertiary amines thus obtained was fractionally distilled as shown in Table VIII.

**Separation of 3,5-Lutidine by Zinc Chloride.**— Industrial grade collidine grade 1 (Sample A) (1250

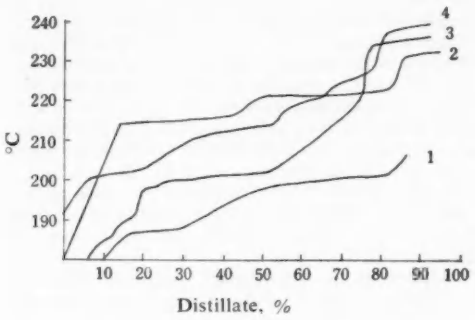



Fig. 8

1 $T_3$ ($S_1$)
2 $X_3$ ($S_1$)
3 Forerunning of quinoline ($S_1$)
4 $X_3$ ($S_4$)

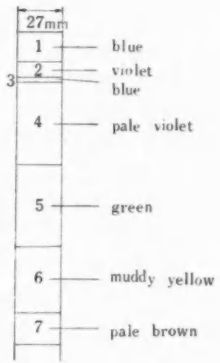



Fig. 9

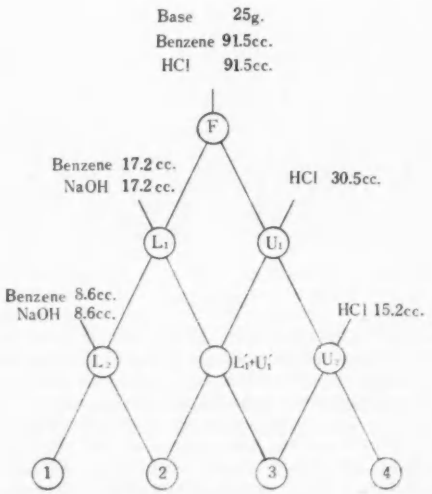



Fig. 10

cc.) was fractionated through a column 2 m. in height and packed with single turn helices, and a fraction boiling at 168~171°C (534 cc.) was obtained. When a 50% aqueous solution of zinc chloride was stirred into this fraction, a white adduct was precipitated which was washed with benzene to remove free bases and then steam-distilled. The distillate, on treatment with an aqueous solution of picric acid, gave crude picrates, m. p. 240°C, in about a 4% yield based on the fraction. The crude picrate (49 g.) was refluxed with 700 cc. of ethanol, yielding 42 g. of pure picrate, which was decomposed to give pure 3,5-lutidine.

**Separation by Urea-adduct.**—*Separation of 2,3,6-Collidine.*—One kilogram of Industrial grade collidine grade 1 (Sample B) was distilled into the following fractions:

| Fraction | up to 165°C | 165~167°C | 170~175°C |
|---|---|---|---|
| Amount, g. | 515 | 107 | 326 |

To the fraction boiling at 170~175°C (80 g.), a 50% aqueous solution of urea was added, and the resulting white adduct of m. p. 128~132°C was decomposed by steam distillation. A picrate (12 g.) melting at 147.4~148.4°C was obtained from the distillate. After being recrystallized once from ethanol, the picrate was decomposed, yielding 3.1 g. of pure 2,3,6-collidine.

*2,3,4,6-Tetramethylpyridine.*—To 16 g. of the fraction ($T_3$) boiling at 200~201°C, 43 g. of a 50% aqueous solution of urea was added, and the resulting adduct was washed with ether and decomposed by steam distillation to give a base (4.5 g.) boiling at 198°C. The picrate of this base, after three recrystallizations from ethanol, melted at 122~122.5°C. The base was also confirmed by picrolonate and ultraviolet absorption spectrum.

*2,3-Cyclopentenopyridine.*—To 36 g. of No. 3 fraction of $X_3$, a solution of urea (112 g.) in 50 cc. of water was added to form urea adduct, m. p. 124~132°C, which was decomposed, yielding 18 g. of basic material showing $n_D^{25}$ 1.5200. This was next purified as picrate, and after a recrystallization from ethanol picrate of 2,3-cyclopentenopyridine (21 g.) which melted at 178~179°C (uncorr.) was obtained. From the filtrate of urea adduct, 10 g. of the picrate of the base was recovered.

*2,3-Cyclopenteno-6-methylpyridine.*—To 5 g. of Nos. 8 and 9 fractions of $S_4$, 1 g. of a 60% aqueous solution of urea was added to yield an adduct from which 2,3-cyclopenteno-6-methylpyridine was recovered as picrate. The purified picrate did not show a melting point depression when admixed with an authentic sample. The results are shown in Table IX.

Similarly, from 50 g. of No. 9 fraction of $S_4$, 19.8 g. of picrate was obtained. The combined picrates were decomposed, yielding 7.45 g. of the free base with $n_D^{35}$ 1.5280. Bases which were recovered from the filtrate of the adduct boiled at 214°C and had $n_D^{20}$ 1.5270, and N content 10.31%.

**Chromatographic Separation.**—*Separation of 3,4,5-Collidine and 2,3-Cyclopenteno-6-methylpyridine.*—As Vignes used for the separation of pyridine, picolines and 2,6-lutidine[6], a mixture of cupric chloride (2 parts), aluminum chloride (25 parts), glycerol (6 parts) and distilled water (2 parts) was ground, dried at 50°C, and then used as an adsorbent in a chromatographic column. The adsorbent (190 g.) was packed in a column as shown in Fig. 9. No. 7 fraction (10.02 g.) from $X_3$, in Table VIII, was placed on a column and developed with 280 cc. of ether. After 5 hr., development was complete, giving various zones as shown in Fig. 9. From each zone, bases were recovered by the addition of an alkali, followed by steam distillation. While examining these bases as picrates, the author found that the bases of Nos. 4 and 5 mainly consisted of 2,3-cyclopenteno-6-methylpyridine, and a base of Nos. 1 and 2 whose picrate melted at 171~172°C (uncorr.) was identified as 3,4,5-collidine (Table X). A comparison of the properties of the base with those of the synthetic sample used in the identification of coal tar bases[10] is as follows: b.p. 210.3~210.8°C (reported 205~207°C), melting point of the picrate 173.6~174.3°C (reported 174°C), N content found 11.25% (Calcd. for $C_8H_{11}N$, 11.52%), molecular weight found 118 (Calcd. 121), and molar refractivity calculated from $d_4^{35}$ 0.9552 and $n_D^{35}$ 1.5115 38.1 (which is very close to the calculated values for collidines 38.6~38.8). The infrared spectrum in carbon disulfide and the ultraviolet spectrum in cyclohexane agreed with those of the literature cited. The base (0.4954 g.) was oxidized with 3.91 g. of potassium permanganate (used as a 2% aqueous solution) at 90°C over a period of 32 hr. Pyridine carboxylic acid was recovered as its copper salt; this was then decomposed by hydrogen sulfide to give the crude acid (0.0874 g.). After a recrystallization from water, pyridine carboxylic acid was obtained which melted with decomposition at 262.5°C (corr.).

Found: N, 5.8. Calcd. for $C_9H_5O_6N \cdot 3H_2O$: N, 5.3%.

*Separation of 2,3,5-Collidine.*—Separation of this base by picrate formation was reported in the literature, but the procedure of recrystallization was time-consuming. By using the chromatographic column described above, 2,3,5-collidine was separated easily. Bases of the fraction boiling at 183~190°C which remained in the solution after the solid urea adduct was removed were placed on the column and developed. A green zone was obtained, and from this zone was recovered a base whose picrate melted at 184~185°C and proved to be 2,3,5-collidine by the mixed melting point. Colors developed by other bases in this procedure are as follows: 3,5-lutidine (blue), 2,4,5-collidine (violet), 2,3,6-collidine (blue) and 2,3-cyclopentenopyridine (blue).

**Separation of 2,3-Cyclopentenopyridine by Countercurrent Extraction.**—2,3-Cyclopentenopyridine which was separated as urea adduct could also be separated by countercurrent extraction. The scheme of extraction, shown in Fig. 10, was similar to that described in the literature[11] using benzene and hydrochloric acid.

Using No. 2 fraction of $S_1$ as a feed, 2,3-cyclopentenopyridine was found to be concentrated in a fraction which was only with great difficulty soluble in the acid phase. The extraction was conducted

11) S. Tanaka et al., *Japan Analyst (Bunseki Kagaku)*, **5**, 455, 513 (1956).

as shown in Fig. 10; bases were distributed between benzene and hydrochloric acid by shaking for 5 min. in a separatory funnel. The upper benzene layer $U_1$ was separated, hydrochloric acid (1 N) was added, and the extraction was repeated, forming upper $U_2$ and lower layer $U_1'$. To $L_1$, which was the lower layer of $U_1$, benzene and 1 N sodium hydroxide were added, and extraction was conducted to give $L_1'$ and $L_2$. $L_1'$ and $U_1'$ were combined and distributed between themselves. The extraction was continued until the 4 fractions shown in Fig. 10 were obtained. The amount, the refractive index and the melting point of the picrate of the base recovered from each fraction are shown in Table XI.

The basicity of the base was expected to decrease gradually from No. 1 to No. 4. From fraction No. 4 the picrate of 2,3-cyclopentenopyridine (4.5 g.) was separated and identified by mixed melting point with an authentic sample.

*Tokyo Laboratory of Research Center*
*Yawata Chemical Industry Co.*
*Chuo-ku, Tokyo*

---

# *The Raman Spectra of 1,3,5-Trichlorobenzene and 1,3,5-Trichlorobenzene-$d_3$*

By Shinnosuke SAËKI

(Received April 12, 1961)

A report on the infrared absorption spectra of ordinary and deuterated 1,3,5-trichlorobenzene has been previously presented by the author[1], but the Raman spectra of these substances have not yet been studied in detail. In this paper the Raman spectra of these substances are reported on, and the assignment of the observed Raman lines is presented, including that of the overtones and combinations.

As the molecule of 1,3,5-trichlorobenzene has a high symmetry, ten pairs of degenerate vibrations are contained in its thirty normal vibrations, and twenty fundamental frequencies are expected to be observed in the molecular spectra of this substance. Of these twenty frequencies, fourteen are active to the Raman effect.

Hitherto the assignments of the normal vibrations of the various aromatic derivatives have been made by collecting a large number of data for many similarly substituted benzenes and by comparing and systematizing these data. In the present report, instead of referring to the data of other substances, the assignment is determined by taking the spectra of both ordinary and deuterated substances, by applying the product rule, and by referring to the results of qualitative measurements of the depolarization ratios.

## Experimental

Commercial 1,3,5-trichlorobenzene was recrystallized from ethanol solution three times, and was then further purified by sublimation. Deuterated material was prepared by stirring the ordinary 1,3,5-trichlorobenzene with deuterated sulfuric acid for eight hours at 105°C. The reaction mixture was poured on ice and recrystallized from ethanol. The progress of substitution was checked by the infrared absorption spectrum after each substitution reaction, and the reaction was repeated until the strongest absorption band of $C_6HD_2Cl_3$ could hardly be recognized. It was found that the absorption bands of $C_6H_3Cl_3$ almost completely disappeared after the first reaction, and that three repetitions of the reaction were sufficient to complete the substitution reaction*.

The instrument used for the measurements was a Cary model 81 Raman spectrophotometer. The source was a mercury arc lamp of Toronto type; the dispersion of the grating was 4 Å/mm. at 5000 Å wavelength.

Raman spectra were taken of the solution in carbon tetrachloride (1 g. solute dissolved in 5 ml. solvent) and in methanol (0.5 g. solute dissolved in 5 ml. solvent) for both ordinary and deuterated substances. As the solubilities of the substances in methanol are not sufficiently large, it was impossible to make the concentration of both solutions equal.

The depolarization ratio was measured by surrounding the Raman tube by polaroid cylinders and by polarizing the exciting light in directions parallel and perpendicular to the axis of the Raman tube.

## Results

The observed Raman spectra are shown in Figs. 1—4. In the spectrum of the methanol solution of ordinary trichlorobenzene, as the base line rose gradually with increasing frequency, it was necessary to reset the zero

1) S. Saëki, This Bulletin, 33, 1024 (1960).

* The substance in which a given band originated was easily known by following the intensity changes of that band with the repetition of the substitution reactions.

suppression of the amplifier at 1800 $cm^{-1}$. Although the cause of the shift of the base line was not found, this gave rise to no obstacle for the measurement of the frequencies of Raman lines. In the figures, the peaks pointed out by the small arrows are due to the solvents or the source lamp (D line, 2602 $cm^{-1}$).

The frequencies and intensities of the observed lines are listed in Tables I and II. The intensities are shown for the spectra excited by the polarized lights in both directions (cross and parallel). The scale of the intensity is simply the height of a Raman line measured on the chart. The notation "masked" in the tables means that the line was not observed in that solution, being masked by a strong Raman line of the solvent, while it was observed in the other solution. The notation "unobserved" means that the line was not observed in that solution, while it was observed

TABLE I. RAMAN SPECTRUM OF 1,3,5-TRICHLOROBENZENE

| $\tilde{\nu}$ $cm^{-1}$ | Methanol soln. intensity | | $\tilde{\nu}$ $cm^{-1}$ | Carbon tetrachloride soln. intensity | | Depolarization ratio |
|---|---|---|---|---|---|---|
| | Cross | Parallel | | Cross | Parallel | |
| 188 | – | 17 | | Masked | | |
| 209 | + | 7 | | Masked | | |
| 373 | 26 | 9 | 374 | 42 | 14 | p. |
| 425 | 5 | 5 | | Unobserved | | |
| | Unobserved | | 526 | 1 | 1 | |
| 994 | 57 | 20 | 994 | 99 | 35 | p. |
| | Masked | | 1060 | 6 | 2 | p. |
| 1147 | 26 | 12 | 1146 | 38 | 15 | p. |
| | Masked | | 1536 | 10 | 3 | |
| 1565 | 12 | 15 | 1565 | 21 | 24 | dep. |
| | Unobserved | | 2150 | 1 | — | |
| | Unobserved | | 2211 | 3 | 0 | |
| | Unobserved | | 2263 | 3 | 1 | |
| 3076 | 17 | 15 | 3081 | 33 | 24 | dep. |
| 3130 | 3 | 0 | 3132 | 7 | 2 | p. |

TABLE II. RAMAN SPECTRUM OF 1,3,5-TRICHLOROBENZENE-$d_3$

| $\tilde{\nu}$ $cm^{-1}$ | Methanol soln. intensity | | $\tilde{\nu}$ $cm^{-1}$ | Carbon tetrachloride soln. intensity | | Depolarization ratio |
|---|---|---|---|---|---|---|
| | Cross | Parallel | | Cross | Parallel | |
| 188 | 70 | 70 | | Masked | | dep. |
| 374 | 38 | 14 | 373 | 63 | 21 | p. |
| 418 | 10 | 10 | 417 | — | 13 | dep. |
| 495 | 5 | 5 | 492 | — | sh. | |
| | Unobserved | | 711 | sh. | sh. | |
| 950 | 86 | 31 | 952 | 100 | 54 | p. |
| | Masked | | 993 | 21 | 6 | p. |
| | Masked | | 1058 | 4 | 1 | |
| 1144 | 18 | 8 | 1142 | 45 | 16 | p. |
| | Masked | | 1337 | 2 | 2 | |
| | Masked | | 1418 | 4 | 1 | |
| | Masked | | 1528 | + | – | |
| 1550 | 25 | 25 | 1548 | 47 | 43 | dep. |
| 1767 | 3 | 2 | | Unobserved | | |
| 1883 | 4 | 3 | | Unobserved | | |
| 2027 | 3 | 3 | | Unobserved | | |
| 2283 | — | 2 sh. | 2282 | sh. | 5 | |
| 2303 | 17 | 10 | 2303 | 41 | 25 | |
| | Unobserved | | 2389 | 2 | 2 | |
| | Unobserved | | 2537 | 6 | 3 | p. |
| | Unobserved | | 3079 | 2 | 2 | |
| | Unobserved | | 3094 | 3 | 2 | |

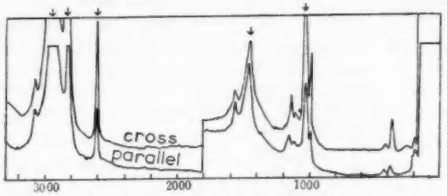



Fig. 1. Raman spectra of 1,3,5-trichlorobenzene (0.5 g. in 5 ml. methanol).

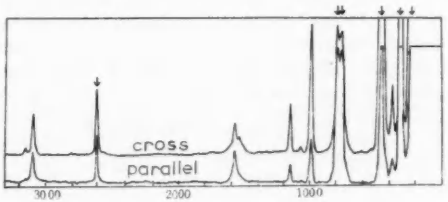



Fig. 2. Raman spectra of 1,3,5-trichlorobenzene (1 g. in 5 ml. carbon tetrachloride).

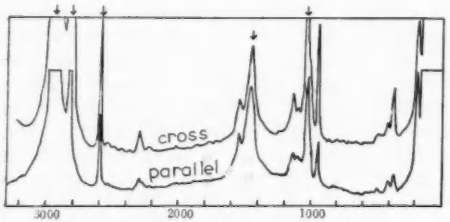



Fig. 3. Raman spectra of 1,3,5-trichlorobenzene-$d_3$ (0.5 g. in 5 ml. methanol).

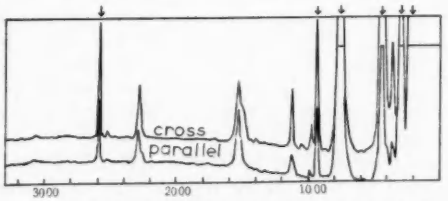



Fig. 4. Raman spectra of 1,3,5-trichlorobenzene-$d_3$ (1 g. in 5ml. carbon tetrachloride).

in the other solution. This inconstancy of observation might be due to the unequal concentrations or to different solvent effects in both solutions. In any case, it should be remembered that there might be a little ambiguity in such lines.

### Assignment

**1, 3, 5-Trichlorobenzene.**—*Species* $A_1'$. — It is universally known that the vibrations belonging to totally symmetric species give the most intense Raman lines. In the case of 1, 3, 5-trichlorobenzene, four normal vibrations belong to species $A_1'$, as is shown in Table III. The C–H stretching vibration is expected to appear about 3000 $cm^{-1}$, the breathing of the benzene ring is expected to appear about 1100 $cm^{-1}$ judging from the case of *p*-dichlorobenzene (which was reported on in our previous paper[2]), the C–Cl stretching vibration is expected to be observed in the region 700~800 $cm^{-1}$, and the deformation of the ring is expected to be observed at 300~400 $cm^{-1}$. From these estimations of the frequencies, four lines with remarkable intensities were selected from the observed Raman lines, that is, the lines at 3079, 1147, 994 and 374 $cm^{-1}$. However, as is seen in Table I, the line at 3079 $cm^{-1}$ was not very definitely polarized. In the vicinity of this line, another line was observed at 3130 $cm^{-1}$ which was apparently polarized. Therefore, it might be considered that this line corresponded to the C–H symmetric stretching vibration of the species $A_1'$ and that the above-mentioned line at 3079 $cm^{-1}$ corresponded to the C–H degenerate stretching vibration of the species E'. But this assignment conflicts with the empirical knowledge that a line belonging to a totally symmetric species is generally more intense than a line belonging to other species, and that the frequency of a degenerate stretching vibration of the C–H bonds is higher than that of a symmetric one as a general rule. Therefore, it seems to be more plausible to assign the line at 3079 $cm^{-1}$ to both degenerate and symmetric stretching vibrations of C–H bonds. Then the line at 3130 $cm^{-1}$ might well be explained as an overtone of the line at 1563 $cm^{-1}$ (e'), which will be discussed later.

The other three polarized lines were easily assigned to the other three normal vibrations

Table III. The normal modes of 1,3,5-trichlorobenzene

| Species | Mode |
|---|---|
| $A_1'$ | C–H or C–D stretching |
| | Ring breathing |
| | C–Cl stretching |
| | Ring deformation |
| E' | C–H or CD stretching |
| | Ring stretching |
| | Ring stretching |
| | C–H or C–D in-plane bending |
| | C–Cl stretching |
| | Ring in-plane deformation |
| | C–Cl in-plane bending |
| E'' | C–H or C–D out-of-plane bending |
| | Ring out-of-plane deformation |
| | C–Cl out-of-plane bending |

2) S. Saëki, ibid., 34, 1658 (1961).

TABLE IV. THE ASSIGNMENTS OF RAMAN LINES OF 1,3,5-TRICHLOROBENZENE

| Species | No. | $\tilde{\nu}$ $C_6H_3Cl_3$ | $\tilde{\nu}$ $C_6D_3Cl_3$ | Mode |
|---|---|---|---|---|
| $A_1'$ | $\nu_1$ | 3079 | 2303 | C-H or C-D stretching |
| | $\nu_2$ | 1147 | 1143 | Ring breathing |
| | $\nu_3$ | 994 | 951 | C-Cl stretching |
| | $\nu_4$ | 374 | 374 | Ring deformation |
| E' | $\nu_{11}$ | 3079 | 2303 | C-H or C-D stretching |
| | $\nu_{12}$ | 1565 | 1548 | Ring stretching |
| | $\nu_{13}$ | (1412) | 1337 | Ring stretching |
| | $\nu_{14}$ | (1103) | (843) | C-H or C-D in-plane bending |
| | $\nu_{15}$ | (814) | (795) | C-Cl stretching |
| | $\nu_{16}$ | 425 | 418 | Ring in-plane deformation |
| | $\nu_{17}$ | 209 or 188 ? | 188 ? | C-Cl in-plane bending |
| E'' | $\nu_{18}$ | — | 711 | C-H or C-D out-of-plane bending |
| | $\nu_{19}$ | 526 | 494 | Ring out-of-plane deformation |
| | $\nu_{20}$ | 188 ? | 188 ? | C-Cl out-of-plane bending |

N. B. The values in parentheses are the wave number which were observed in the infrared spectra.

of species $A_1'$, as is shown in Table IV. Since these lines had remarkable intensities, and no alternate lines were observed in their vicinities, the assignment was quite unambiguous. Although the frequency of the $\nu_3$, the C-Cl stretching vibration, to which the line at 994 $cm^{-1}$ was assigned, was a little higher than the expected value, it is nevertheless a quite probable value for such a vibration, considering the fact pointed out in our previous paper[3] that the strong coupling between the normal vibrations of such frequencies may often cause a large frequency shift from the empirically expected one. Consequently, this molecule might not have a normal vibration which could be called a C-Cl stretching vibration in its proper sense. However, at present such a vibration will be called a C-Cl stretching vibration for convenience.

*Species E'.* — Contrary to the easy assignment of the normal vibrations belonging to species $A_1'$, the assignment of the observed lines to the seven normal vibrations of this species was very difficult. Since the normal vibrations belonging to species E' are active in both the Raman and infrared spectra, the assignments would appear to be easily achieved by looking for the frequencies which were commonly observed in the Raman and infrared spectra. However, this could not be done so easily in practice. Actually only four frequencies were commonly observed in Raman and infrared spectra, that is, 3079 (3098), 1565 (1565), 1060 (1100 or 1055) and 425 (430). (in $cm^{-1}$. The frequencies put between parentheses are those observed in the infrared absorption spectrum in a gaseous state.) The fact that only four vibrations appeared commonly in both spectra, while seven were expected, suggested that the intensities of the Raman lines or the infrared absorption bands of the other three vibrations were to weak to be observed. But, on the other hand, the abovementioned four lines could definitely be assigned to species E'. However, the line at 1060 $cm^{-1}$ was somewhat questionable. Since the infrared absorption spectrum of the substance was measured in the gaseous state, the frequency of an observed band must be a little higher than that of the corresponding line observed in the Raman spectrum. From this consideration, it was not reasonable to consider the infrared absorption band at 1055 $cm^{-1}$ to correspond to the Raman line at 1060 $cm^{-1}$. And the other infrared band observed at 1103 $cm^{-1}$ seemed too high to be regarded as the corresponding band of this Raman line. Moreover, its depolarization ratio shown in Table I suggested that it belongs to species $A_1'$. These facts might rule out the assignment of the line at 1060 $cm^{-1}$ to the normal vibration of species E'.

As for the other three commonly observed frequencies, the line at 3079 $cm^{-1}$ was assigned to the degenerate stretching vibration of C-H bonds ($\nu_{11}$), as was mentioned above, and the line at 1565 $cm^{-1}$ was assigned to the stretching vibration of the benzene ring ($\nu_{12}$), and the line at 425 $cm^{-1}$ to the deformation vibration of the benzene ring ($\nu_{16}$), all with sufficient certainty.

As for the remaining four normal vibrations

3) S. Saëki, ibid., 33, 1021 (1960).

of this species ($\nu_{13}$, $\nu_{14}$, $\nu_{15}$ and $\nu_{17}$), the assignment of the lines was very difficult. The stretching vibration of the benzene ring, $\nu_{13}$, is empirically expected to appear in the frequency region 1400~1600 $cm^{-1}$. But, as is seen in Fig. 1 and in Table I, no Raman line was clearly observed in this region except for the line at 1565 $cm^{-1}$. A weak line observed only with difficulty at 1536 $cm^{-1}$ for the solution in carbon tetrachloride was polarized and had to be considered as an overtone or a combination belonging to species $A_1'$ (for example 1147 ($a_1'$)+374($a_1'$)). As was already reported in our previous paper[1], the infrared absorption spectrum of this substance showed many intense absorption bands in this region of the spectrum (1412 (s), 1398 (m), 1384 (m) and 1341 (s)). The band at 1412 $cm^{-1}$ was especially clearly assigned to a fundamental because of its outstanding intensity. Consequently, although the Raman line was not observed, it appears to be plausible to assign this band to $\nu_{13}$.

The C–H in-plane bending vibration was expected to appear in the vicinity of 1000 $cm^{-1}$, where only the above-mentioned polarized line at 1060 $cm^{-1}$ was observed. In the infrared absorption spectrum[1], a remarkable band was observed at 1103 $cm^{-1}$ which showed a large frequency shift on the substitution for hydrogen atoms by deuterium atoms. Accordingly, we assigned this band to the C–H in-plane bending vibration ($\nu_{11}$).

As for the C–Cl stretching vibration $\nu_{15}$, since the coupling with other vibrational modes might shift its frequency from its usual value, as in the case of $\nu_3$, it would be necessary to examine it over a relatively wide region of frequency, such as 600~1000 $cm^{-1}$. However, no Raman line was found in spite of taking such an extremely wide region. In the infrared absorption spectrum, two intense bands were observed, that is, bands at 855 and 814 $cm^{-1}$. The former was clearly identified from the shape of its envelope* to be a band which did not belong to species E'. Consequently, the band at 814 $cm^{-1}$ was assigned to the C–Cl stretching vibration of species E' ($\nu_{15}$).

The C–Cl in-plane bending vibration $\nu_{17}$ was expected to be found about 200 $cm^{-1}$. In the neighborhood of 200 $cm^{-1}$ a remarkable line was observed at 188 $cm^{-1}$, and a less intense line was observed at 209 $cm^{-1}$. Since there exists another Raman active bending vibration of C–Cl bonds which belongs to species E'' (out-of-plane), the above-mentioned two observed Raman lines apparently originate in these two C–Cl bending vibrations. However, it was difficult to find the correspondence between these lines and these normal vibrations. It was imagined, by analogy to C–H vibrations, that the line of the higher frequency (209 $cm^{-1}$) might probably correspond to the in-plane bending vibration, and the lower one to the out-of-plane vibration. Of course, however, this was not certain.

*Species E''.*—Three out-of-plane normal vibrations belong to this species, as listed in Table III. To the C–Cl out-of-plane bending vibration $\nu_{20}$, as was mentioned above, either the line at 209 $cm^{-1}$ or the line at 188 $cm^{-1}$ —probably the latter—was to be assigned. The out-of-plane deformation vibration of the benzene ring $\nu_{19}$ was expected to be observed from 400 to 500 $cm^{-1}$, where a very weak and depolarized line was found at 526 $cm^{-1}$. Disregarding its low intensity, we assigned this line to $\nu_{19}$ for the following reasons: 1. An overtone or combination belonging to a species other than $A_1'$ might not appear in the spectrum with an observable intensity. 2. The frequency of this line (526 $cm^{-1}$) could not be derived by combining or multiplying the frequencies of other fundamentals. 3. The line at 1060 $cm^{-1}$ which was mentioned in previous paragraphs was well explained as the overtone of this line.

The C–H out-of-plane vibration $\nu_{18}$ was expected to appear in the vicinity of 800 $cm^{-1}$, but no corresponding Raman line was observed in this frequency region. This might be because the intensity of the line was probably too low to be observed.

*Overtones and Combinations.*—The overtones and combinations which have already been explained are as follows:

3132 $cm^{-1}$ ($A_1'$): 1565 $cm^{-1}$ (e')×2

1536 $cm^{-1}$ ($A_1'$): 1147 $cm^{-1}$ ($a_1'$)
+374 $cm^{-1}$ ($a_1'$) three weak lines

1060 $cm^{-1}$ ($A_1'$): 526 $cm^{-1}$ (e'')×2

In addition to these lines three weak lines were observed between 2100 and 2300 $cm^{-1}$, as is shown in Table I. Though two of these lines were easily explained as

2263 $cm^{-1}$ ($A_1'$): 1147 $cm^{-1}$ ($a_1'$)×2

2211 $cm^{-1}$ ($A_1'$): 1103 $cm^{-1}$ (e')×2

the third line observed at 2150 $cm^{-1}$ was difficult to explain. It might probably originate. in a slight amount of impurity.

The assingment determined above is shown in Table IV.

**1, 3, 5-Trichlorobenzene-$d_3$.**—*Species $A_1'$.*—The strong and polarized Raman line at 2303 $cm^{-1}$

* Concerning the envelopes of the infrared absorption bands of these substances, a report will be presented soon.

was easily and definitely assigned to the symmetric stretching vibration of C–D bonds. The remaining three vibrations are the breathing and the deformation of the benzene ring, and the symmetric stretching of the C–Cl bonds, all of which are not much influenced by the substitution for hydrogen atoms by deuterium atoms. Therefore, these vibrations of deuterated 1, 3, 5-trichlorobenzene were expected to be observed at frequencies only a little lower than those of the corresponding lines of 1, 3, 5-trichlorobenzene, that is, at 1147, 994 and 374 $cm^{-1}$ respectively. In fact, as is shown in Table II, three strong and polarized lines were found at 1143, 951 and 374 $cm^{-1}$ in the Raman spectra of deuterated trichlorobenzene. So, the lines at 1143, 951 and 374 $cm^{-1}$ were unambiguously assigned to the ring breathing ($\nu_2$), C–Cl stretching ($\nu_3$) and ring deformation vibration ($\nu_4$) respectively. In the Raman spectrum of deuterated substance, a line was observed at 993 $cm^{-1}$ which appeared to correspond to the line at 994 $cm^{-1}$ of ordinary substance better than the line at 951 $cm^{-1}$ did. However, the requirement of fulfilling the product rule and the definite inferiority in the intensity of the line at 993 $cm^{-1}$ to the line at 951 $cm^{-1}$ ruled out the assignment of the former line to $\nu_3$. It seemed that this line should be explained as the overtone of the line at 492 $cm^{-1}$ ($e''$), which will be discussed later, just as the line at 1060 $cm^{-1}$ was the overtone of the line at 526 $cm^{-1}$ in the case of ordinary substance. Its unusually strong intensity might well be explained by the Fermi resonance with the line at 951 $cm^{-1}$.

*Species* $E'$. — As was done in the case of ordinary substance, four frequencies which were observed commonly in the Raman and infrared absorption spectra were picked up. These were 2303 (2310), 1548 (1560), 1337 (1342) and 418 (420)$cm^{-1}$. The line at 2303 $cm^{-1}$ was a polarized line and was already assigned to the C–D symmetric stretching vibration of species $A_1'$. In the neighborhood of this line was observed another weak depolarized line at 2282 $cm^{-1}$. It was difficult to determine which of these two lines was to be assigned to the C–D degenerate stretching vibration. However, since the line at 2282 $cm^{-1}$ might be explained as a combination, 952 ($a_1'$)+1342 ($e'$, gaseous infrared band), the line at 2303 $cm^{-1}$ was assigned to the C–D degenerate stretching vibration, assuming that its frequency was equal to that of the symmetric vibration as in the case of trichlorobenzene.

The lines at 1548 and at 418 $cm^{-1}$ were assigned to the stretching and deformation vibrations of the benzene ring respectively. As these line definitely corresponded to the lines at 1565 and 425 $cm^{-1}$ of ordinary substance, there is no point of discussion in the assignment.

The line at 1337 $cm^{-1}$, though weak in Raman spectra, corresponded to the intense band at 1342 $cm^{-1}$ in the infrared absorption spectrum, and it was plausibly assigned to the stretching vibration of the ring, $\nu_{13}$, by taking account of its frequency and depolarization ratio. Other weak lines observed in its vicinity, that is, lines at 1528, 1455 and 1418 $cm^{-1}$, could not be assigned to $\nu_{13}$ from a consideration of their depolarization ratios and of correspondencies with the infrared absorption bands.

The remaining three vibrations are the in-plane bending vibration of C–D bonds, the stretching vibration and the in-plane bending vibration of C–Cl bonds. As the first two vibrations were not observed in the Raman spectra, probably because of their weak intensities, as in the case of trichlorobenzene, the frequencies of observed in the infrared spectrum had to be adopted. To the in-plane bending vibration of C–D bonds was assigned the absorption band at 843 $cm^{-1}$ observed in the infrared spectrum, for the corresponding band of the ordinary substance was observed at 1103 $cm^{-1}$. The absorption band at 799 $cm^{-1}$ was assigned to the C–Cl stretching vibration, because the band at 814 $cm^{-1}$ was assigned to the corresponding vibration of ordinary substance.

The in-plane bending vibration of C–Cl bonds was expected to be observed near 200 $cm^{-1}$, and only a remarkable line at 188 $cm^{-1}$ was observed in this region for deuterated substance. From both the intensity and the depolarization ratio, this line was considered to correspond to the line at 188 $cm^{-1}$ of ordinary substance, but it was not known at this point whether this line was to be assigned to the in-plane or to the out-of-plane vibration of C–Cl bonds. Concerning this alternate assignment, some discussion will be given later.

*Species* $E''$. — The frequency of the out-of-plane bending vibration of C–D bonds is estimated to be lower than 800 $cm^{-1}$, and a diffuse line was observed at 711 $cm^{-1}$ as a shoulder of a strong Raman line of the solvent in the spectrum of carbon tetrachloride solution of deuterated substance. This line seemed to be recognizable also in the methanol solution, but due to its low intensity it could not be clearly distinguished from the noise. However, a polarized line which seemed to correspond to the first harmonic of this vibration was observed at 1418 $cm^{-1}$. Since this line could not be explained as an overtone or as a combination of other vibrations, the line at 711 $cm^{-1}$ could be considered as a normal vibration.

It was apparent from the frequency and

the depolarization ratio that the line at 494 $cm^{-1}$ corresponds to the line at 526 $cm^{-1}$ of ordinary substance. Accordingly the line at 494 $cm^{-1}$ was assigned to the out-of-plane bending vibration of the benzene ring of deuterated substance.

As for the out-of-plane vibration of C–Cl bonds, the line at 188 $cm^{-1}$ might be assigned to it. However, as was mentioned above, it is difficult to determine whether this line is to be assigned to the in-plane or out-of-plane vibration of C–Cl bonds.

The above assignment is shown in Table IV.

*Overtones and Combinations.*—More overtones and combinations were observed in the spectra of deuterated substance than in that of ordinary substance. As was stated above, the line at 993 $cm^{-1}$ was explained as 495 ($e''$)×2, the line at 2282 $cm^{-1}$ as 952 ($a_1'$)+1337 ($e'$), and the line at 1418 $cm^{-1}$ as 711 ($e''$)×2. For the other observed Raman lines, the following explanations were possible:

1058: 535 ($a_2''$)×2

1455: ?

1528: 1337 ($e'$, from the infrared spectrum) +188 ($e'$ or $e''$)

1767: 1337 ($e'$)+418 ($e'$)

1883: 1143 ($a_1'$)+767 ($e'$) or 1337 ($e'$) +535 ($a_2''$)

2029: 1550 ($e'$)+841 ($e'$, from the infrared spectrum)

2537: 950 ($a_1'$)+1550 ($e'$)

3079, 3094: 1549 ($e'$)×2, 2303 ($a_1'$ and $e'$) +801 ($a_2''$)

Though the line observed at 1455 $cm^{-1}$ could not be well explained, the existence of such a line is quite natural, since the molecule has three normal vibrations belonging to species $A_2'$ which are active to neither the Raman nor the infrared spectrum. Some of the above-mentioned explanations of overtones and combinations were not consistent with the observed qualitative depolarization ratios* But this inconsistency might not be very significant. If too much confidence was put in the observed results of the depolarization ratio, it might sometimes lead to an erroneous assignment. However, it should be mentioned here that the above explanation of the overtones and combinations may not be absolutely correct because of the existence of the unobservable normal vibrations.

## Discussion

The product rule was applied to the assignment given above. For species $A_1'$, the ratio of the products of the frequencies of the ordinary and deuterated trichlorobenzenes was calculated from the observed frequencies, such as 1.401 in good agreement with the theoretical value 1.414, showing that the assignment was correct.

In species $E'$, it has previously been pointed out that the assignment of $\nu_{17}$ was somewhat questionable. The theoretical value of the ratio is 1.982. Assuming that the line at 209 $cm^{-1}$ of ordinary trichlorobenzene and the line at 188 $cm^{-1}$ of deuterated correspond to the in-plane bending vibrations of C–Cl bonds, $\nu_{17}$'s, the ratio calculated from the observed frequencies was 2.162, exceeding the theoretical value by about 9%. On the other hand, assuming that the line observed at 188 $cm^{-1}$ of both trichlorobenzenes corresponds to $\nu_{17}$, the calculated ratio was found to be 1.944, lower than the theoretical value by about 2%. This discrepancy of 2% could be expected from the accumulation of small errors in frequency measurements, from the shift of the fundamental lines due to Fermi reasonance, etc., but that of 9% had to be regarded as inexplicable and might suggest an erroneous assignment. Thus, it was decided that the lines at 188 $cm^{-1}$ in both substances had to be assigned to $\nu_{17}$. However, it should be mentioned here that, since there exists a possibility that an unobservably weak line corresponding to the line at 209 $cm^{-1}$ does exsist at a suitable frequency (about 205 $cm^{-1}$) in the spectrum of deuterated substance, the above assignment can not be considered absolutely correct.

For species $E''$, the theoretical value is 1.402. However, since $\nu_{18}$ (C–H out-of-plane bending vibration) of ordinary trichlorobenzene was not observed, the observed ratio could not be compared with the theoretical one. Accordingly, the above-mintioned question concerning the assignment of the C–Cl in-plane bending vibration could not be solved. However, if the frequency of $\nu_{20}$'s were assumed to be 188 $cm^{-1}$ for both ordinary and deuterated substances, the frequency of $\nu_{18}$ of ordinary substance could be calculated to be 936 $cm^{-1}$ by applying the product rule. However, as was stated in the previous paragraphs, no Raman line was observed in the neighborhood of this frequency.

* For example, the combination of two fundamental vibrations belonging to species $E'$ brings out four vibrations belonging to species $A_1'$, $A_2'$ and $E'$ respectively, of which the one belonging to species $A_1'$ might have the highest intensity in Raman effect. Therefore, the depolarization ratio of the observed line corresponding to this combination has to be considerably small.

**Summary**

The Raman spectra and the qualitative depolarization ratio of each line were observed for the solutions of 1, 3, 5-trichlorobenzene and 1, 3, 5-trichlorobenzene-$d_3$. The assignments of Raman active normal vibrations of these substances were carried out from the results of these measurements. The assignments for species $A_1'$ and $E'$ proved to be correct from the application of the product rule, showing a good accordance between theoretical and calculated ratios of products of the frequencies. However, the application of the product rule was impossible for species $E''$ because of unobserved frequencies.

The author would like to express his appreciation of the valuable advice given by Dr. Y. Mashiko.

*Government Chemical Industrial Research Institute, Tokyo*
*Shibuya-ku, Tokyo*

---

# *Raman Spectra of 1, 2, 4, 5-Tetrachlorobenzene and 1, 2, 4, 5-Tetrachlorobenzene-$d_2$*

By Shinnosuke SAËKI

(Received May 16, 1961)

Concerning the infrared absorption spectra of 1, 2, 4, 5-tetrachlorobenzene and 1, 2, 4, 5-tetrachlorobenzene-$d_2$, a report[1] was previously presented by the author in which tentative assigments were proposed for the observed infrared absorption bands. In this paper the Raman spectra of these substances will be presented, and the assignment of these observed lines will be discussed.

The Raman spectra of ordinary 1,2,4,5-tetrachlorobenzene have already been reported on by several investigators[2]. But all of their papers have been concerned with a group of similarly substituted benzenes, 1, 2, 4, 5-tetrachlorobenzene was treated simply as a member of this group. Consequently, the molecular spectra of 1, 2, 4, 5-tetrachlorobenzene itself do not appear to have been fully studied. In this paper, instead of adopting such an inductive method, the Raman spectrum was observed for deuterated as well as for ordinary 1, 2, 4, 5-tetrachlorobenzene, and the assignment was carried out by comparing the Raman spectra for both species of the substance.

Since the molecule contains four chlorine atoms, the normal vibrations were expected to be concentrated in a lower frequency region compared with those of *p*-dichlorobenzene and 1, 3, 5-trichlorobenzene, which have been studied in previous papers[3-6]. As the observation of low frequency vibrations is much easier in Raman effect than in infrared spectroscopy, the product rule can be applied more completely to Raman lines. However, since a Raman line belonging to a species other than the totally symmetric one generally has a relatively low intensity and can often escape observation, this might become a new obstacle for the assignment.

## Experimental and Results

Ordinary commercial 1,2,4,5-tetrachlorobenzene of extra pure grade was recrystallized from ethanol three times, and then further purified by sublimation.

The deuterated substance was prepared in the following way: 1,2,4,5-tetrachlorobenzene was stirred with deuterated sulfuric acid for eight hours at 150°C. The reaction mixture was then poured on ice and the precipitate filtered off and dried. The degree of substitution was checked by the infrared absorption spectrum after each substitution reaction, and the reaction was repeated until the strongest absorption band of $C_6HDCl_4$ could hardly be recognized. The obtained $C_6D_2Cl_4$ was purified in the same way as that of ordinary tetrachlorobenzene.

The Raman spectra were measured by using a Cary model 81 automatic recording spectrophotometer, and the qualitative depolarization ratios were measured by the two-exposure method, using polaroid cylinders.

The measurements were carried out for the solutions in carbon tetrachloride and in benzene.

Although the Raman spectra of *p*-dichlorobenzene and 1,3,5-trichlorobenzene were measured for the solutions in methanol and carbon tetrachloride[5,6], the solubility of 1,2,4,5-tetrachlorobenzene in

1) S. Saëki, This Bulletin, **34**, 1552 (1961).
2) For example, J. W. Murray and D. H. Andrews, *J. Chem. Phys.*, **2**, 119 (1934).
3) S. Saëki, This Bulletin, **33**, 1021 (1960).
4) S. Saëki, ibid., **33**, 1024 (1960).
5) S. Saëki, ibid., **34**, 1658 (1961).
6) S. Saëki, ibid., **34**, 1851 (1961).

methanol is so low that the spectra could not be measured in methanol solutions. Since the solubility of chlorobenzene decreases with the increasing number of chlorine atoms contained in the molecule, the concentrations of the sample solutions were not very high in this case. In the carbon tetrachloride solution, about 0.7 g. solute was dissolved in 5 ml. of solvent, while in the benzene solution about 0.6 g. solute was dissolved in 5 ml. of solvent. Irrespective of these low concentrations, the solute was not entirely dissolved at room temperature, and it was necessary to keep the Raman tube in the lamp compartment for almost an hour in order to dissolve the entire solute*.

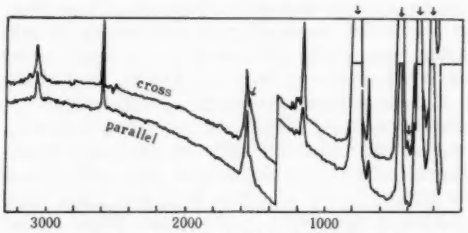


Fig. 1. Raman spectra of 1,2,4,5-tetrachlorobenzene (0.7 g. in 5 cc. carbon tetrachloride).

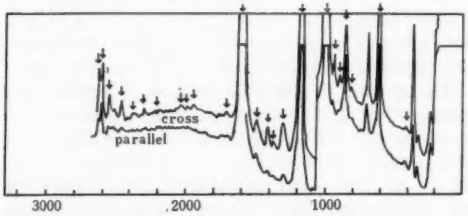


Fig. 2. Raman spectra of 1,2,4,5-tetrachlorobenzene (0.6 g. in 5 cc. benzene).

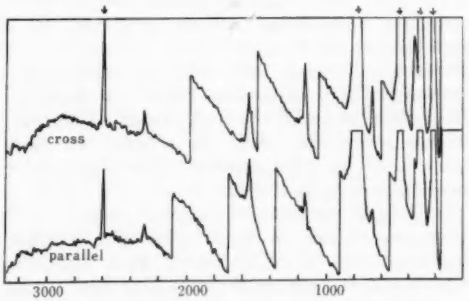


Fig. 3. Raman spectra of 1,2,4,5-tetrachlorobenzene-$d_2$ (0.5 g. in 4 cc. carbon tetrachloride).

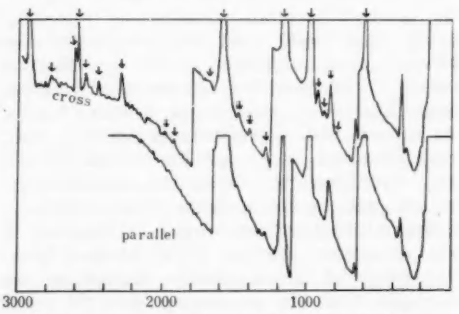


Fig. 4. Raman spectra of 1,2,4,5-tetrachlorobenzene-$d_2$ (0.6 g. in 5 cc. benzene).

TABLE I. RAMAN SPECTRUM OF 1,2,4,5-TETRACHLOROBENZENE

| Carbon tetrachloride solution | | | Benzene solution | | |
|---|---|---|---|---|---|
| | Intensity | | | Intensity | |
| $\tilde{\nu}$, cm$^{-1}$ | Cross | Parallel | $\tilde{\nu}$, cm$^{-1}$ | Cross | Parallel |
| | | | 184 | sh 1 | sh 1 |
| | | | 226 | 16 | 17 |
| | | | 314 | 10 | 12 |
| 350 | >70 | sh 22 | 352 | 84 | 38 |
| | | | 467 | 1 | – |
| | | | 509 | 2 | 2 |
| ca. 570 | 2 | – | 554 | 1 | — |
| 685 | 50 | 18 | 685 | 53 | 22 |
| 1162 | 72 | 27 | | | |
| 1190 | 7 | 6 | | | |
| 1206 | 10 | 5 | | | |
| 1236 | 3 | 3 | | | |
| ca. 1535 | + | – | | | |
| 1567 | 33 | 35 | | | |
| 2502 | 6 | 3 | | | |
| 3075 | 25 | 17 | | | |
| 3137 | 4 | – | | | |

TABLE II. RAMAN SPECTRUM OF 1,2,4,5-TETRACHLOROBENZENE-$d_2$

| Carbon tetrachloride solution | | | Benzene solution | | |
|---|---|---|---|---|---|
| | Intensity | | | Intensity | |
| $\tilde{\nu}$, cm$^{-1}$ | Cross | Parallel | $\tilde{\nu}$, cm$^{-1}$ | Cross | Parallel |
| | | | 184 | sh 2 | sh 4 |
| | | | 215 | sh 5 | sh 7 |
| | | | 315 | 6 | 7 |
| 351 | 63 | sh 20? | 351 | 49 | 22 |
| 667 | 41 | 16 | 665 | 34 | 14 |
| | | | 956 | sh 10 | |
| 1155 | 54 | 21 | | | |
| 1180 | 6 | 5 | | | |
| 1208 | 4 | + | | | |
| 1410 | 2? | – | | | |
| 1418 | 7 | 2 | | | |
| 1520 | 1? | sh + | | | |
| 1552 | 44 | 45 | | | |
| 1675 | 3? | – | | | |
| 2301 | 17 | 13 | | | |
| ca. 2500 | 6 | + | | | |

* The temperature was 36°C in the lamp compartment.

As the concentrations of the solutions were low, a relatively high gain was required for the measurements; consequently, the signal to noise ratio in the obtained spectra was about 25, a rather low value for this spectrometer. The obtained Raman spectra are shown in Figs. 1—4, where the noises could not be well represented because of the small sizes of the figures. The base line of each spectrum, especially of the spectra of deuterated substance, rose towards the higher frequency limit of the spectrum. This was probably due to a slight amount of resinous impurity, which was unavoidable in this case. The rapid rising of the base line made necessary its resetting at several frequencies, but it produced no obstruction to the measurement of the frequencies of Raman lines.

In the figures, the Raman lines marked with small arrows are those of the solvent or of the mercury arc lamp.

The observed Raman lines are listed in Tables I and II. In the tables, the intensities are simply represented by the heights of lines measured by the scale on the chart.

## Assignment

Since the 1, 2, 4, 5-tetrachlorobenzene molecule has the symmetry $V_h$, as does the *p*-dichlorobenzene molecule, fifteen of thirty normal vibrations are active to the Raman effect. Also, as this molecule has a center of symmetry, there is no vibration which is active in both the Raman effect and infrared absorption, according to the mutual exclusion law. The fifteen Raman active normal vibrations are classified as six vibrations belonging to species $A_g$ (in-plane), five to species $B_{3g}$ (in-plane), one to species $B_{1g}$ (out-of-plane), and three to species $B_{2g}$ (out-of-plane)*. These normal vibrations and their modes are shown in Table III.

TABLE III. SPECIES AND MODES OF NORMAL VIBRATIONS OF 1,2,4,5-TETRACHLOROBENZENE

| Species | No. | Mode |
|---|---|---|
| $A_g$ | $\nu_1$ | C-H or C-D stretching |
| | $\nu_2$ | Ring stretching |
| | $\nu_3$ | Ring stretching |
| | $\nu_4$ | C-Cl stretching |
| | $\nu_5$ | Ring deformation |
| | $\nu_6$ | C-Cl in-plane bending |
| $B_{1g}$ | $\nu_9$ | C-Cl out-of-plane bending |
| $B_{2g}$ | $\nu_{15}$ | C-H or C-D out-of-plane bending |
| | $\nu_{16}$ | Ring out-of-plane deformation |
| | $\nu_{17}$ | C-Cl out-of-plane bending |
| $B_{3g}$ | $\nu_{23}$ | Ring stretching |
| | $\nu_{24}$ | C-H or C-D in-plane bending |
| | $\nu_{25}$ | C-Cl stretching |
| | $\nu_{26}$ | Ring in-plane deformation |
| | $\nu_{27}$ | C-Cl in-plane bending |

* The x-axis was taken along the two-fold axis perpendicular to the molecular plane, and the z axis was taken along the line combining the two hydrogen atoms.

Sixteen Raman lines were observed for ordinary as well as for deuterated 1, 2, 4, 5-tetrachlorobenzene, but, considering their frequencies, some of them apparently do not correspond to normal vibrations. Therefore, it seems that some of the Raman active normal vibrations were not observed on account of very low frequencies or intensities.

**1, 2, 4, 5-Tetrachlorobenzene.** — *Species $A_g$.* — The six normal vibrations belonging to species $A_g$ are seen in Table III. In the spectra obtained, the polarized and strong lines were observed in the regions expected from their modes, except for $\nu_2$ and $\nu_6$ (see Figs. 1 and 2), and the following assignment was unambiguously decided upon: $\nu_1$: 3075 $cm^{-1}$, $\nu_3$: 1162 $cm^{-1}$, $\nu_4$: 685 $cm^{-1}$ and $\nu_5$: 350 $cm^{-1}$. Considering the high intensities and low depolarization ratios of these lines, no point of discussion exists in the above assignment.

In the region around 1500 $cm^{-1}$ where the ring stretching vibration was expected to appear, a remarkable line was observed at 1567 $cm^{-1}$. However, the large depolarization ratio of this line clearly showed itself to correspond to the ring stretching vibration of species $B_{3g}$. In addition to this line, a much weaker line was with difficulty observed at 1535 $cm^{-1}$ only in the carbon tetrachloride solution. As this line was observed as a shoulder of the Raman line of the solvent at 1550 $cm^{-1}$ only in the spectrum excited by perpendicularly polarized light, its accurate frequency was difficult to measure. However, it was clear that this was a polarized line, since it entirely disappeared when excited by parallelly polarized light.

It might be indeed unusual for a line belonging to species $A_g$ to show such a weak intensity, but since no other polarized line was found in this region, this line had to be considered to correspond to the totally symmetric ring stretching vibration.

As for the last vibration of species $A_g$, $\nu_6$, the in-plane bending vibration of the C-Cl bonds, two weak lines were observed near 200 $cm^{-1}$, one at 226 $cm^{-1}$ and the other at 184 $cm^{-1}$. In the carbon tetrachloride solution, these lines were masked by a strong line of the solvent, but in the benzene solution they were observed as a shoulder of the exciting line. However, neither of these lines could be assigned to $\nu_6$, for both of them had considerable depolarization ratios. Therefore, it was concluded that $\nu_6$ might have a lower frequency and be completely masked by the Rayleigh line. By estimating from the width of the Rayleigh line, the frequency should be lower than 175 $cm^{-1}$.

*Species $B_{1g}$.*—As is seen in Table III, the only vibration belonging to species $B_{1g}$ is the out-of-plane bending vibration of C–Cl bonds, $\nu_9$. As there are four Raman active bending vibrations of C–Cl bonds, that is, $\nu_6$, $\nu_9$, $\nu_{17}$ and $\nu_{27}$, it is very difficult to determine the assignment of the two observed lines at 184 and 226 $cm^{-1}$. However, these lines were shifted to 184 and 215 $cm^{-1}$ respectively, by the deuteration; this fact suggests that the line at 226 $cm^{-1}$ of ordinary tetrachlorobenzene could not correspond to $\nu_9$, which belongs to species $B_{1g}$, for the product rule requires that the ratio of the $\nu_9$'s of ordinary and deuterated tetrachlorobenzene be 1. Consequently, the conclusion was drawn that the vibration $\nu_9$ corresponds to the line at 184 $cm^{-1}$ or lies in the unobservable low frequency region.

*Species $B_{2g}$.*—Although the out-of-plane bending vibration of C–H bonds was expected to appear in the region from 800 to 1000 $cm^{-1}$, no Raman line was observed in this region, as is seen in Table I. Since the Raman active out-of-plane vibrations of C–H bonds were not observed in the spectrum of *p*-dichloro- and 1, 3, 5-trichlorobenzene, as was reported in the previous papers[2,3], it appeared to be unobservable, in this case also on account of its low intensity.

To the out-of-plane deformation vibration of the ring, $\nu_{16}$, the line at 314 $cm^{-1}$ could be assigned. However, since there is another ring deformation vibration belonging to species $B_{3g}$ ($\nu_{26}$), it seemed also possible to assign the line at 314 $cm^{-1}$ to it. However, this latter possibility must be ruled out for a reason which will be mentioned later.

As for the out-of-plane bending vibration of C–Cl bonds, $\nu_{17}$, it is possibly unobserved. However, provided that it were observed in the spectra, the line at 184 $cm^{-1}$ or 226 $cm^{-1}$ might be regarded as the corresponding line.

*Species $B_{3g}$.*—As the stretching vibration of the benzene ring, $\nu_{23}$, was expected to appear at about 1500 $cm^{-1}$, it was clear that the above-mentioned remarkable line at 1567 $cm^{-1}$ corresponded to this vibration. This assignment is consistent with the observed qualitative depolarization ratio.

In the region 1000~1200 $cm^{-1}$ where the in-plane bending vibration of C–H bonds, $\nu_{24}$, was expected to appear, two lines of medium intensity were observed at 1190 and 1206 $cm^{-1}$. Since the latter line was polarized, as is shown in Table I, the former was assigned to $\nu_{24}$.

Although the C–Cl stretching vibration, $\nu_{25}$, was expected to appear in the vicinity of 700 $cm^{-1}$, no line was observed in this region except the strong line at 685 $cm^{-1}$ which had already been assigned to $\nu_4$. But if lines are looked for over a wider frequency region, two weak lines are found at 509 and 554 $cm^{-1}$. Although the former was a little stronger than the latter, the latter combining with the line at 685 $cm^{-1}$ ($a_g$), gave a combination line at 1236 $cm^{-1}$ which could not be explained as any other combination. Therefore, the line at 554 $cm^{-1}$ was assigned to $\nu_{25}$.

To the in-plane deformation vibration of the benzene ring, $\nu_{26}$, either the line at 467 $cm^{-1}$ or at 509 $cm^{-1}$ might be assigned. It appeared to be a little strained to assign the line at 314 $cm^{-1}$ to $\nu_{26}$, for $\nu_{26}$ probably has a frequency higher than 351 $cm^{-1}$, which was the frequency of the totally symmetric in-plane deformation vibration of the benzene ring. However, since the lines at 467 and 509 $cm^{-1}$ were both very weak, it was difficult to determine which was to be assigned to $\nu_{26}$. If one was taken for the fundamental, the other had to be explained as an overtone or a combination. However, if necessary, both of them could be explained as an overtone or a combination, that is, $467=226$ ($b_{2g}$) $\times 2$ and $509=184$ ($b_{1g}$ or $b_{3g}$) $+314$ ($b_{2g}$).

However, there was another, more plausible explanation for the line at 509 $cm^{-1}$. As was reported in our previous paper[4], a strong absorption band was observed at 507 $cm^{-1}$ in the infrared absorption spectrum of this substance. Taking account of this fact, the Raman line at 509 $cm^{-1}$ was explained as the forbidden line which was brought out by the breakdown of the rule of mutual exclusion in solution. Since it is quite probable that the rule of mutual exclusion breaks down in the condensed system, the above explanation appeared to be the most plausible. Accordingly, the line at 467 $cm^{-1}$ was assigned to $\nu_{26}$.

For the C–Cl in-plane bending vibration, $\nu_{27}$, there were two lines to be assigned, that is, the lines at 184 $cm^{-1}$ and at 226 $cm^{-1}$. As has been mentioned above, it is impossible to determine definitely the assignment of these lines. It might as possibly be that $\nu_{27}$ was not observed as that $\nu_{27}$ corresponds to one of these two lines.

*Overtones and Combinations.*—There were five observed lines which were not assigned to the fundamentals, that is, the lines at 3137, 2502, 1236, 1206 and 509 $cm^{-1}$. The lines at 1236 and 509 $cm^{-1}$ have already been explained as 685 ($a_g$) $+554$ ($b_{3g}$) and as a forbidden line which was brought out by the breakdown of the mutual exclusion law respectively.

The line at 3137 $cm^{-1}$ was clearly explained as 1567 ($b_{3g}$) $\times 2$.

Although the lines at 2502 and 1206 $cm^{-1}$ were both polarized, these could be well explained neither as an overtone nor as a combination belonging to species $A_g$. Since these

two lines were observed also in the carbon tetrachloride solution of the deuterated substance, as is shown in Table II, they should be regarded as lines due to the slight impurity contained in the solvent. Although these lines were not observed in the Raman spectrum of the pure solvent, they might quite probably appear in the spectra of sample solutions because of the extremely high gain required on the measurement of the sample solutions. Thus, these lines were removed from discussion.

**1, 2, 4, 5-Tetrachlorobenzene-$d_2$.**—*Species $A_g$.*—The line at 2301 $cm^{-1}$ corresponded apparently to $\nu_1$, the stretching vibration of the C–D bonds. Although the depolarization ratio of this line was observed to be unusually high*, there was no other remarkable line in its vicinity. Since there is no other Raman active stretching vibration of C–D bonds, there is no room for doubting this assignment.

A very weak line observed at 1520 $cm^{-1}$ was assigned to $\nu_2$, for it was apparent from the frequency and the intensity that this line corresponds to the line at 1535 $cm^{-1}$ ($\nu_2$) of ordinary 1, 2, 4, 5-tetrachlorobenzene.

For $\nu_3 \sim \nu_5$, the assignment could unambiguously be determined, as is shown in Table IV. No line was observed for $\nu_6$. This might be because its frequency was too low to be observed, as in the case of ordinary substance. A combination line was observed at 1675 $cm^{-1}$ which could well be explained by assuming the frequency of $\nu_6$ to be 155 $cm^{-1}$, as will be shown later. But, of course, this was not strong enough support for assigning 155 $cm^{-1}$ to $\nu_6$.

*Species $B_{1g}$.*—Only $\nu_9$ belongs to this species. As was already mentioned, it is not certain that the frequency of this vibration is high enough to be observed. Provided that this vibration can be observed, the line at 184 $cm^{-1}$ could be assigned to it.

*Species $B_{2g}$.*—The C–D out-of-plane bending vibration of this species, $\nu_{15}$, was not observed as in the case of the ordinary substance.

To the deformation vibration of the ring, $\nu_{16}$, the line at 315 $cm^{-1}$ was assigned. Although it is impossible that the frequency of the deuterated substance is higher than that of the ordinary substance (314 $cm^{-1}$), this might be attributed to a slight error in the measurement of the frequency because of excessive noise.

As for $\nu_{17}$, the line at 184 $cm^{-1}$ might be assigned to it. However, the assignment for such C–Cl bending vibrations is not very certain for the reason which has already been stated in the case of ordinary tetrachlorobenzene.

* The measurement was repeated three times, and the high depolarization ratio was observed every time.

*Species $B_{3g}$.*—The line at 1552 $cm^{-1}$ was easily assigned to $\nu_{23}$, the stretching vibration of the ring.

As for $\nu_{24}$, since it was observed at 1190 $cm^{-1}$ in the case of the ordinary substance, it was expected to appear near 1000 $cm^{-1}$ in the deuterated substance. But in this region only a weak and diffuse line was observed at 956 $cm^{-1}$. Since, irrespective of its low depolarization ratio, this line could not be explained as an overtone or as a combination belonging to species $A_g$, it might be assigned to $\nu_{24}$. It will be seen later that this assignment facilitates the explanation of some combination lines.

Although $\nu_{25}$ and $\nu_{26}$ of ordinary tetrachlorobenzene were observed at 554 and 467 $cm^{-1}$ respectively, those of deuterated one were not observed.

As for $\nu_{27}$, since the line at 226 $cm^{-1}$ was assigned to it in the case of 1, 2, 4, 5-tetrachlorobenzene, the line at 215 $cm^{-1}$ should be assigned to it in the case of deuterated substance.

*Overtones and Combinations.*—There were six observed lines which were not assigned to the fundamentals, that is, 1180, 1208, 1410, 1448, 1675 and 2500 $cm^{-1}$. Of these six, the two lines at 1208 $cm^{-1}$ and 2500 $cm^{-1}$ should be regarded as lines of the impurity contained in the solvent (carbon tetrachloride), as was pointed out in the previous paragraphs, and removed from discussion.

The line at 1180 $cm^{-1}$ was explained as 956 ($b_{3g}$) + 215 ($b_{2g}$). The existence of this combination line appeared to justify not only the assignment of the weak line at 956 $cm^{-1}$ to a fundamental, but also the determination of species $B_{2g}$ for the fundamental line at 215 $cm^{-1}$. For, by assuming that this line corresponds to the fundamental of species $B_{3g}$ ($\nu_{27}$), the species of the combination line at 1180 $cm^{-1}$ should be $A_g$, while the observed depolarization ratio was relatively high. However, it should be mentioned here that the certainty of this determination of the species depends on the reliability of the measurement of the depolarization ratio.

The lines at 1410 and 1448 $cm^{-1}$ were well explained as the overtones of the infrared active fundamentals of 719 and 725 $cm^{-1}$ respectively. These two overtones might perhaps resonate and be shifted away from each other.

The line at 1675 $cm^{-1}$, with a low depolarization ratio, could not be explained as an overtone, but, provided that the frequency of the unobserved $\nu_6$ of species $A_g$ is 155 $cm^{-1}$, it can be explained as a combination, 1520 ($a_g$) + 155 ($a_g$).

The assignments determined above are shown in Table IV.

TABLE IV. THE ASSIGNMENTS OF RAMAN LINES OF ORDINARY AND DEUTERATED 1,2,4,5-TETRACHLOROBENZENE

| Species | No. | $\tilde{\nu}$ | | Mode |
|---|---|---|---|---|
| | | $C_6H_2Cl_4$ | $C_6D_2Cl_4$ | |
| $A_g$ | $\nu_1$ | 3075 | 2301 | C-H or C-D stretching |
| | $\nu_2$ | ca. 1535 | 1520 | Ring stretching |
| | $\nu_3$ | 1162 | 1155 | Ring stretching |
| | $\nu_4$ | 685 | 667 | C-Cl stretching |
| | $\nu_5$ | 351 | 351 | Ring in-plane deformation |
| | $\nu_6$ | — | — | C-Cl in-plane bending |
| $B_{1g}$ | $\nu_9$ | 184? | 184? | C-Cl out-of-plane bending |
| $B_{2g}$ | $\nu_{15}$ | — | — | C-H or C-D out-of-plane bending |
| | $\nu_{16}$ | 314 | 315 | Ring out-of-plane deformation |
| | $\nu_{17}$ | 226 | 215 | C-Cl out-of-plane bending |
| $B_{3g}$ | $\nu_{23}$ | 1567 | 1552 | Ring stretching |
| | $\nu_{24}$ | 1190 | 956 | C-H or C-D in-plane bending |
| | $\nu_{25}$ | 554 | — | C-Cl stretching |
| | $\nu_{26}$ | 467 | — | Ring in-plane deformation |
| | $\nu_{27}$ | 184? | 184? | C-Cl in-plane bending |

## Discussion

According to the product rule, the theoretical values of the product of the ratios of the frequencies for each substance are 1.414, 1, 1.393 and 1.408 for species $A_g$, $B_{1g}$, $B_{2g}$ and $B_{3g}$ respectively.

For species $A_g$, although the frequencies of $\nu_6$'s were observed for neither species of substance, these could with enough security be assumed to be nearly equal*. With this assumption, the ratio calculated from the observed frequencies for species $A_g$ was 1.394 in good accordance with the above-mentioned theoretical value, showing the correctness of the proposed assignment.

For species $B_{1g}$, the assignment was determined so that the product rule might be fulfilled.

For species $B_{2g}$, as the bending vibrations of C-H and C-D bonds were not observed, the application of the product rule was impossible.

For species $B_{3g}$, the application of the product rule was also impossible because, while all normal vibrations were observed for 1,2,4,5-tetrachlorobenzene (assuming that $\nu_{27}$ is 184 $cm^{-1}$), some of those for 1,2,4,5-tetrachlorobenzene-$d_2$ were not observed.

Generally speaking, in the case of 1,2,4,5-tetrachlorobenzene, it was difficult to observe Raman lines of low intensity because of its poor solubility to the solvents. Furthermore, it is impossible, because of the mutual exclusion law, to look for these unobserved normal frequencies in the infrared absorption spectrum. Consequently, for some of the normal vibrations of this substance, there was no way of knowing their frequencies; this fact prevented the application of the product rule to verify the proposed assignment for most of the species. However, the clear explanation of observed weak lines as overtones or combinations appears to suggest that the proposed assignments might be the most reliable one at present.

* The fact that the normal vibrations with low frequency were scarcely influenced by the substitution for hydrogen atoms of deuterium ones has been seen in the cases of *p*-dichlorobenzene and 1,3,5-trichlorobenzene (Refs. 5 and 6).

## Summary

The Raman spectra of 1,2,4,5-tetrachlorobenzene and 1,2,4,5-tetrachlorobenzene-$d_2$ were measured in their dissolved states in methanol and carbon tetrachloride. The depolarization ratio of each Raman line was also observed qualitatively by the two-exposure method, using polaroid cylinders. On the basis of these experimental results, the assignment of normal vibrations was determined. The verification of the proposed assignments by means of the product rule was impossible for most of the species because of some unobserved normal vibrations. But, for species $A_g$, good agreement was obtained between the theoretical and observed values of the product of the frequencies for each substance, and the correctness of the assignment was thus verified.

The author would like to thank Dr. Y. Mashiko for helpful comments in connection with this paper.

*Government Chemical Industrial Research Institute, Tokyo*
*Shibuya-ku, Tokyo*

# *Mass-spectrometric Study on Ionization and Dissociation of Formaldehyde, Acetaldehyde, Acetone and Ethyl Methyl Ketone by Electron Impact*

By Ichiro KANOMATA

(Received March 28, 1961)

The ionization and dissociation of ethyl alcohol[1,2] and diethyl ether[3] molecules caused by electron impact have previously been studied by the present author. It has been concluded that the ionization takes place by the removal of one of the lone pair electrons of the oxygen atom and that the bond energy additivity can be applied to the ionized dissociation of these molecules by considering the trivalent character of the $O^+$.

In this report, the ionization and dissociation of formaldehyde, acetaldehyde, acetone and ethyl methyl ketone molecules, each of which has an oxygen atom as in the case of alcohols and ethers, are discussed in relation to the determination of appearance potentials of the ions produced by electron impact. In the case of formaldehyde and acetaldehyde, Reed[4,5] previously carried out an appearance potential study for the purpose of determining the dissociation energies of $D$(H–CHO), $D$(H–CO) and $D$($CH_3$–CHO) and the ionization potential of CHO radical. Further, Morrison et al.[6] reported the determination of the ionization potentials of these two molecules. A similar study was also made by Kambara[7] with acetone.

## Experimental

The mass-spectrometer[8] used for this study is of a 90° sector type ($r$=12 cm.). The appearance potentials (AP) of ions were determined by the retarding potential difference method[9] (RPD). The apparatus[10] is nearly identical with Fox's[11], and its details have been described[12]. The ionization potentials and uppor break points on the ionization efficiency curves of $N_2$, CO and Kr obtained in the present study agree well with Fox's results.

The ionization potential of argon (15.77 eV.) was used as a standard for parent ions, although, owing to the RPD method, such a standard was not necessary in as much as the ion source was clean. Appearance potentials of fragment ions were determined by referring to the appearance potentials of parent ions.

The samples were chemically pure. Formaldehyde was prepared through the thermal decomposition of the polymer, and other sample gases were used after dehydration by calcium chloride.

## Results

The appearance ratios of the ions produced by 75 eV. electron impact and their appearance potentials are shown in Tables I and II respectively. Some ionization efficiency curves are illustrated in Fig. 1. Owing to the RPD method, characterized by a narrow distribution (0.2 eV.) of electron energy, fine structures appear in the ionization efficiency curves.

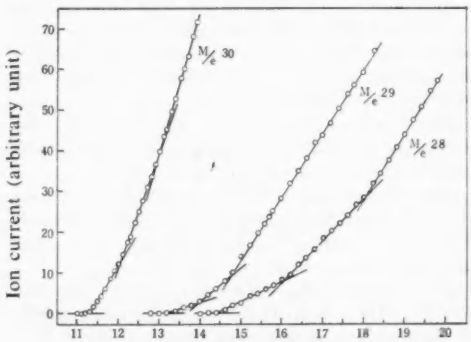



Fig. 1. Ionization efficiency curves of $HCHO^+$, $CHO^+$ and $CO^+$.

## Discussion

The production processes of ions are as follows:

*1) Formaldehyde*

**M/e=30** $HCHO^+$

The ion is a parent ion. Two distinct breaks exist in the ionization efficiency curve; the

1) T. Kambara and I. Kanomata, *Butsuri*, **4**, 71 (1949).
2) T. Kambara and I. Kanomata, *Hitachi Hyoron Rombun-shu*, No.7, 15 (1949).
3) I. Kanomata, This Bulletin, **34**, 1596 (1961).
4) R. E. Reed, *Trans. Faraday Soc.*, **53**, 1195 (1957).
5) R. E. Reed, ibid., **54**, 949 (1958).
6) H. Hurzeler, M. G. Inghram and J. D. Morrison, *J. Chem. Phys.*, **28**, 76 (1958).
7) T. Kambara, *J. Phys. Soc. Japan*, **5**, 84 (1950).
8) I. Kanomata, Y. Kaneko and T. Oguri, *Mass Spectroscopy*, No. 3, 12 (1954).
9) R. E. Fox, W. M. Hickam, T. Kjeldaas and D. J. Grove, *Phys. Rev.*, **84**, 859 (1951).
10) I. Kanomata, Y. Kaneko and T. Oguri, *Mass Spectroscopy*, No. 6, 46 (1956).
11) R. E. Fox et al., *Rev. Sci. Instr.*, **26**, 1101 (1955).
12) I. Kanomata, Y. Kaneko and T. Oguri, *J. Appl. Phys. Japan*, **30**, 502 (1961).

TABLE I. APPEARANCE RATIO

| M/e | Ion | Appearance ratio | | | |
|---|---|---|---|---|---|
| | | $(CH_3)(C_2H_5)CO$ | $(CH_3)_2CO$ | $CH_3CHO$ | HCHO |
| 72 | $C_4H_8O^+$ | 53.0 | | | |
| 58 | $C_3H_6O^+$ | | 37.4 | | |
| 57 | $C_3H_5O^+$ | 22.4 | 1.3 | | |
| 45 | $C_2H_5O^+$ | 0.5 | | | |
| 44 | $C_2H_4O^+$ | 2.4 | 2.3 | 64.5 | |
| 43 | $C_2H_3O^+$ | **100.0** | **100.0** | 37.8 | |
| 42 | $C_2H_2O^+$, $C_3H_6^+$ | 6.5 | 4.8 | 10.7 | |
| 41 | $C_2HO^+$, $C_3H_5^+$ | 2.4 | 2.4 | 4.8 | |
| 40 | $C_2O^+$, $C_3H_4^+$ | 1.2 | 1.3 | | |
| 39 | $C_3H_3^+$ | 4.3 | 3.7 | | |
| 38 | $C_3H_2^+$ | 2.4 | 1.8 | | |
| 37 | $C_3H^+$ | 2.3 | 1.4 | | |
| 30 | $CH_2O^+$ | 4.5 | | | 90 |
| 29 | $CHO^+$, $C_2H_5^+$ | 20.2 | 3.3 | **100.0** | **100** |
| 28 | $CO^+$, $C_2H_2^+$ | 7.4 | 14.6 | 13.4 | 29.8 |
| 27 | $C_2H_3^+$ | 5.4 | 4.8 | | |
| 26 | $C_2H_2^+$ | 1.3 | 3.1 | 7.1 | |
| 25 | $C_2H^+$ | | 7.7 | | |
| 16 | $CH_4^+$, $O^+$ | | | 7.0 | |
| 15 | $CH_3^+$ | 23.7 | 19.6 | 44.5 | |
| 14 | $CH_2^+$ | 5.1 | 2.7 | 16.0 | 5 |
| 13 | $CH^+$ | 1.6 | | 5.0 | 4 |
| 12 | $C^+$ | 1.7 | | | 3 |

TABLE II. APPEARANCE POTENTIAL (eV.)

| M/e | Ion | Appearance potential | | | |
|---|---|---|---|---|---|
| | | $(CH_3)(C_2H_5)CO$ | $(CH_3)_2CO$ | $CH_3CHO$ | HCHO |
| 72 | $(CH_3)(C_2H_5)CO^+$ | $9.88\pm0.03$, $10.5_3$ | | | |
| 58 | $(CH_3)_2CO^+$ | | $9.84\pm0.04$<br>$10.6_7\pm0.1$<br>$11.5_4\pm0.1$ | | |
| 57 | $C_2H_5CO^+$ | $10.81\pm0.04$, 12.0 | | | |
| 44 | $CH_3CHO^+$ | | | $10.31\pm0.04$<br>$11.2_4\pm0.1$<br>12.2 | |
| 43 | $CH_3CO^+$, $CH_2CHO^+$ | $11.10\pm0.03$, 12.4 | $10.94\pm0.04$<br>$11.9_4\pm0.1$<br>$12.9_4\pm0.1$ | $11.38\pm0.04$<br>$12.0_5\pm0.1$<br>$12.7\pm0.1$<br>$13.7\pm0.1$ | |
| 30 | | | | | $10.86\pm0.02$<br>$11.6_6\pm0.1$<br>$12.6_3\pm0.15$ |
| 29 | $C_2H_5^+$, $CHO^+$ | $12.71\pm0.03$, 15.2 | | $12.53\pm0.04$<br>$13.8\pm0.15$<br>$14.8\pm0.2$<br>$16.9\pm0.2$ | $12.90\pm0.07$<br>$13.6\pm0.1$<br>$14.2_5\pm0.1$ |
| 28 | $CO^+$, $C_2H_4^+$ | $14.4\pm0.2$, 15.6<br>17.4 | $14.6\pm0.2$<br>15.4<br>16.8 | $14.5_4\pm0.1$<br>15.3~15.6<br>$17.4\pm0.2$ | $14.1\pm0.05$<br>15.5~15.9<br>$18.3\pm0.3$ |
| 27 | $C_2H_3^+$ | | 16.9 | | |
| 15 | $CH_3^+$ | $15.4\pm0.2$ | $15.53\pm0.08$<br>$17.3\pm0.15$ | $14.8_2\pm0.05$ | |

energy values corresponding to the threshold and the breaks are 10.86±0.02, $11.6_6$±0.1 and $12.6_3$±0.15 eV. respectively. Sugden and Price[13] determined the first, second and third ionization potentials of HCHO as 10.8±0.1, 11.8±0.2 and 13.1±0.2 eV. respectively through the measurement of the total ion current produced by the impact of accelerated photo-electrons. The three values obtained by the present author may be expected to correspond to these ionization potentials.

The first ionization potential of 10.86 eV. agrees well with Reed's result of 10.85 eV. obtained by electron impact[4], with Watanabe's of 10.87 eV. by photon impact[14], and with the spectroscopic value of 10.88 eV.[15] It was pointed out by McMurry[16] in his report on absorption spectra that lone pair electrons of the oxygen atom in the molecule are at the highest occupied orbital. Therefore, the first ionization potential corresponds to the energy necessary for the removal of one of the lone pair electrons.

The second ionization potential of $11.6_6$ eV., on which there are very few data[13], may relate to the ionization caused by the removal of the $\pi$-electron of the C–O bond, as has been theoretically pointed out by Foster and Boys[17] and by Sugden.

The third ionization potential of $12.6_3$ eV. is thought to correspond to the removal of a $\sigma$-electron from the C–O bond, as has also been pointed out by Foster and Boys.

The values of the first ionization potentials of parent molecules of aldehyde and ketone obtained by the present author are listed in Table III with their dipole moments. It is shown that the ionization potentials decrease by 0.5 eV. in the order of HCHO, $CH_3CHO$ and $(CH_3)_2CO$, but that the ionization potential of $(CH_3)(C_2H_5)CO$ is a little larger than that of $(CH_3)_2CO$.

TABLE III. IONIZATION POTENTIAL AND DIPOLE MOMENT

| Molecule | Ionization potential, eV. | Dipole moment* ($D$) |
|---|---|---|
| HCHO | 10.86 | 2.27 |
| $CH_3CHO$ | 10.31 | 2.72 |
| $C_2H_5CHO$ | — | 2.73 |
| $(CH_3)_2CO$ | 9.84 | 2.85 |
| $(CH_3)(C_2H_5)CO$ | 9.88 | 2.79 |

* Dipole moment: Compiled by L. G. Wesson, a publication of the Technology press. M.I.T.

13) T. M. Sugden and W. C. Price, *Trans. Faraday Soc.*, **44**, 116 (1948).
14) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).
15) W. C. Price, ibid., **3**, 256 (1935).
16) H. L. McMurry, ibid., **9**, 231 (1941).
17) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960).

The fact that ionization potentials decrease with the increase of the number of $CH_3$ group may be due to the effect of hyper-conjugation on the ionization of the oxygen atom. That is, it is considered, in general, that the hyper-conjugation effect is predominant when the carbon atom bound with the $CH_3$ group is in an $sp^2$ configuration. The fact that the ionization potential of ethyl methyl ketone is somewhat larger than that of acetone seems to indicate that the hyper-conjugation plays an important role in the present case.

These results closely relate to the change of the dipole moments of the molecules which can be explained by the hyper-conjugation. The ionization potential decreases with the increment of dipole moment.

**M/e=29** $H–C\equiv O^+$

Two breaks exist in the ionization efficiency curve of this ion. The values of the threshold and the breaks are 12.90, 13.6 and $14.2_5$ eV. respectively.

The appearace potential of the $R_1^+$ ion produced from the $R_1R_2$ molecule is expressed as follows when excess energy (excitation and kinetic energy of $R_1^+$ and/or $R_2$) is disregarded.

$$A(R_1^+)=I(R_1)+D(R_1-R_2)$$

If the ionization takes place by the removal of one of the lone pair electrons belonging to the oxygen atom in the molecule, the energy necessary for this reaction is 10.86 eV. By inserting the value of $D$(H–CHO) (79.3 kcal./mol. or 3.45 eV.) in the above equation, the ionization potential of $R_{29}$ is obtained as 9.45 eV. (12.9 eV.−3.45 eV.). This value is 1.4 eV. lower than the ionization potential of the formaldehyde molecule. This may be explained by the fact that the triple bond formation can be expected between C and $O^+$ in the ionized state of CHO, while, for the ionized state of formaldehyde, only the double bond can exist. That is, the formation of the triple bond brings the stabilization of 1.4 eV. on the $CHO^+$. The value of 1.4 eV. is considerably smaller than the stabilization energy of 2.35 eV. in the case of $H_2C=O^+-C_2H_5$ produced from diethyl ether[3].

The bond energy between C and O in formaldehyde is 144 kcal./mol.[18] If it is assumed that this bond energy is not affected by the ionization of the lone pair electron of the oxygen atom in the molecule, the total bond energy of $O^+$ in the $CHO^+$ is calculated as 176.2 kcal./mol. (144 kcal./mol. + 23.06 × 1.4 kcal./mol.).

18) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond", Interscience Publishers, New York.

The author has previously pointed out in his discussion of the ionized decomposition of diethyl ether[3] that the total bond energies of $O^+$ in $H_2C=O^+-C_2H_5$ and in $H-C\equiv O^+$ are 204 kcal./mol. and 183 kcal./mol. respectively. The present datum (176 kcal./mol.) agrees with the previous result (183 kcal./mol.) on the whole.

The reason why the energy of trivalence in the $H-C\equiv O^+$ is smaller than that in the $H_2C=O^+-C_2H_5$ is thought to be due to the fact that the former has a smaller number of resonance structures.

**M/e=28 $CO^+$**

The observed appearance potentials of this ion are 14.1±0.05, 15.5~15.9 and 18.3±0.3 eV. respectively.

The following two processes may be considered for the creation of $CO^+$ from formaldehyde:

$$HCHO+e \rightarrow CO^+ [19]+H_2+2e$$

$$HCHO+e \rightarrow CO^+ +2H+2e$$

The heat of reaction, or the appearance potential of $CO^+$, is calculated as 14.1 eV. for the former reaction and as 18.5 eV. for the latter. These values agree well with the appearance potentials obtained in the present work.

The break between 15.5~15.9 eV. in the ionization efficiency curve is vague; it sometimes appears, and sometimes it dose not. The value is close to the ionization potential of the nitrogen molecule, so it is thought that the break is due to the ionization of $N_2$, which exists as a background in the mass-spectrometer.

On the other hand, from the thermal decomposition experiments previously made by the present author, it has been found that HCHO is thermally unstable, that it decomposes easily to the CO molecule, and that the CHO radical can not be expected through the thermal decomposition. Therefore, it is also reasonable to consider that a part of formaldehyde gas thermally decomposes into CO gas on the tungsten filament of the ion source and that the CO molecule is ionized when it enters again into ionization chamber. According to this assumption, the first appearance potential of M/e=28 corresponds to the ionization potential of the CO molecule; the experimental result does not disagree with the above conclusion. In this case, the second breaks at 18.3 eV. may correspond to the excited state of the $CO^+$ ion.

19) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions", Academic Press Inc. Publishers, New York (1957).

*2) Acetaldehyde*

**M/e=44 $CH_3CHO^+$**

The observed value of 10.31 eV. is the first ionization potential of the acetaldehyde molecule. Two breaks exist, at $11.2_4$ and 12.2 eV. on the ionization efficiency curve.

Sugden and Price[13] have previously obtained observed values of 10.4±0.1, 11.3±0.1, 12.3±0.1 and 13.5±0.2 eV. through measurement of the total ionization current. The first three values agree well with the values of the present author. At the electron energy as large as 13.5 eV., the dissociation of molecular ion certainly takes place. So Sugden's method, which dealt with only the total ionization current, is unsuitable for the determination of the higher ionization potentials of the parent molecule.

As regards the classification of the ionization potentials of $CH_3CHO$, it is reasonable to consider, as in the case of $HCHO^+$, that 10.31 eV. corresponds to the energy necessary for the removal of one of the lone pair electrons of the oxygen atom in the molecule, that $11.2_4$ eV. is the energy needed for the removal of a $\pi$-electron in the C–O bond, and that 12.3 eV. is the energy needed for the removal of an $\sigma$-electron in the C–O bond in the molecule.

**M/e=43 $CH_3CO^+$ or $CH_2CHO^+$**

The appearance potential of this ion is 11.38 eV., and breaks exist at 12.1, 12.7 and 13.7 eV. The M/e=43 ion is produced by subtracting a hydrogen atom from the parent molecular ion. The bond dissociation energy of C–H in the aldehyde radical is thought to be smaller than that in the methyl radical; moreover, if a hydrogen atom is removed from the aldehyde radical, the stabilization of energy due to the formation of a triple bond of $O^+$ may take place. Accordingly it is reasonable to conclude that the hydrogen atom is removed from the aldehyde radical in the molecule. Thus, when relation $A(R43^+)=I(R43)+D(CH_3CO-H)$ and $D(CH_3CO-H)=3.48$ eV.[20] are used, $I(CH_3CO)$ is obtained as 7.90 eV.

This value is 2.41 eV. (55 kcal./mol.) smaller than the ionization potential of the parent molecule. It can be considered that the stabilization by 2.41 eV. takes place with the formation of a triple bond of $O^+$ in this ion. If it is assumed that the bond energy between C and O atoms in acetaldehyde is not affected by the ionization of one of the lone pair electrons of oxygen atom and that the bond energy additivity is applicable to such an ionic state, the total bond energy of $O^+$ in $CH_3C\equiv O^+$ is

20) J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

obtained as 204.5 kcal./mol. (149.5+55 kcal.) by considering that the bond energy between C and O in acetaldehyde is 149.5 kcal.[18]

On the other hand, the total bond energy of $O^+$ in $CHO^+$ was calculated as 176 and 183 kcal. by the author, as has been described above. The increase of the stabilization in the $CH_3CO^+$ ion seems to be due to the resonance between different structures, for example, $H_3{\equiv}C{-}C{\equiv}O^+$ and $H^+H_2{-}C{=}O$.

As for the second and the third ionization potentials, no information has been obtained to interpret them.

**M/e=29** $CHO^+$

As $D(CH_3{-}CHO)$[20] is 71.5 kcal./mol. (3.10 eV.), $I(CHO)$ is calculated as 9.43 eV. from the observed appearance potential of the ion. This value agrees well with the value of $I(CHO)$ obtained from HCHO in this report, and it is only a little smaller than Reed's value of 9.87 eV.[4] In this case the stabilization energy is obtained as follows:

$I(CH_3CHO)-I(CHO)=0.88$ eV. (20.4 kcal./mol.). Therefore, the total bond energy of $O^+$ in $H{-}C{\equiv}O^+$, calculated under the assumptions described above, is 170 kcal./mol. (149.5 +20.4 kcal./mol.). This value should more closely agree with the 183 kcal./mol. obtained from diethyl ether and with the 176 kcal./mol. from formaldehyde. However, such a discrepancy among these values is unavoidable under these loose assumptions.

**M/e=28** $CO^+$ or $C_2H_4^+$

The ionization efficiency curve of M/e=28 has an uncertain break between 15.3~15.6 eV. and a rather distinct break at 17.4 eV. The heat of reactions, or the appearance potentials of $CO^+$ from $CH_3CHO$, are obtained, by considering the heat of the formation of $CO^+$ and of the other related molecules and radicals, as follows:

$$CH_3CHO+e \rightarrow CO^+ + CH_4 + 2e \quad 13.8\text{ eV.}$$
$$CH_3CHO+e \rightarrow CO^+ + CH_2 + H_2 + 2e \quad 15.8\text{ eV.}$$
$$CH_3CHO+e \rightarrow CO^+ + H + CH_3 + 2e \quad 18.2\text{ eV.}$$

The calculated values do not agree with the observed appearance potentials of the M/e=28 ion. However, as the appearance ratio of this ion is very small the influence of $N_2^+$ from the background in the mass-spectrometer could be expected to be greater, and so the apparent appearance potentials should also be greater than expected. By considering such a bad observing condition, the observed values may be said to correspond closely enough to the above-estimated reactions.

On the other hand, if the reaction is assumed as $CH_3CHO \rightarrow C_2H_4^+ + O$, the heat of reaction would be 15.3 eV.

**M/e=15** $CH_3^+$

The reaction to produce $CH_3^+$ is supposed as

$$CH_3CHO+e \rightarrow CH_3^+ [19] + CHO + 2e$$
or $$CH_3CHO+e \rightarrow CH_3^+ + CO + H + 2e$$

The ionization potential of $CH_3$ radical can be estimated from various data. The mean value of the data given from various ionized decompositions of organic compounds is 10.0 eV. Moreover, the energy for direct ionization of $CH_3$ radical is also 10.0 eV. If $I(CH_3)=10.0$ eV., $D(CH_3-CHO)=3.10$ eV.[20] and $D(H-CO)=1.13$ eV.[20], the heat of reaction for these processes is calculated as 13.10 eV. and 14.23 eV. respectively. The observed value agrees with the latter calculated value by assuming that the reaction has an excess energy of 0.6 eV.

*3) Acetone*

**M/e=58** $(CH_3)_2CO^+$

Two break points exist in the ionization efficiency curve. The values of the threshold and the break points are 9.84±0.04, $10.6_7$±0.1 and $11.5_4$±0.1 eV. respectively. It is thought that these values must be compared with Sugden and Price's values, 10.2±0.1, 11.3±0.1, 12.2±0.1 and 13.6±0.2 eV., which were obtained by the measurement of the total ionization current produced by the impact of accelerated photo-electrons. The discrepancy is large. Sugden's method seems, however, to be unsuitable for the determination of the higher ionization potentials of the parent molecule because of the formation of fragment ions. The first ionization potential of the molecule was determined as 9.92 and 9.89 eV. mass-spectrometrically, by Morrison et al.[21] and Omura et al.[22] respectively, as 9.69 eV. from the measurement of the total ionization current produced by photon impact by Watanabe[23], and as 9.705 eV. spectrometrically. It is reasonable that the first, second and third ionization potentials obtained are correlated, as in the case of formaldehyde, to the ionization of the lone pair electron of the oxygen atom, of the $\pi$-electron and of the $\sigma$-electron in the C-O bond respectively.

**M/e=43** $CH_3CO^+$

There are two breaks in the ionization efficiency curve. By considering that $D(CH_3-COCH_3)$ is 3.15 eV.[20], $I(CH_3CO)$ is obtained as

21) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).
22) I. Omura, K. Higasi and H. Baba, This Bulletin, **29**, 504 (1956).
23) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

7.79 eV. from the relation of $I(CH_3CO) = A(CH_3CO^+) - D(CH_3-COCH_3)$. The value is 2.05 eV. smaller than the ionization potential of acetone. By assuming the structure of this ion as $CH_3C{\equiv}O^+$, in which the trivalency is satisfied, the value of 2.05 eV. is thought to be the stabilization energy through the formation of the triple bond.

The total bond energy of $O^+$ in the ion is calculated as 202 kcal./mol. by adopting 155 kcal./mol.[18] as the bond energy between C and O in acetone. The value 202 kcal./mol. agrees well with that calculated in the case of acetaldehyde.

**M/e=28** $CO^+$ or $C_2H_4^+$

The appearance ratio of this ion is small, and the influence of $N_2^+$ in background seems to be large, so the accuracy is not great. The heat of reaction for seven processes, which are all expected to produce M/e=28, is calculated as follows:

$(CH_3)_2CO+e \rightarrow CO^+$ [19] $+C_2H_6+2e$ 14.3 eV.

$(CH_3)_2CO+e \rightarrow CO^+ + H_2 + C_2H_4 + 2e$ 15.7 eV.

$(CH_3)_2CO+e \rightarrow CO^+ + 2(CH_3) + 2e$ 17.9 eV.

$(CH_3)_2CO+e \rightarrow C_2H_4^+$ [19] $+CO+H_2+2e$ 12.2 eV.

$(CH_3)_2CO+e \rightarrow C_2H_4^+ + HCHO + 2e$ 12.1 eV.

$(CH_3)_2CO+e \rightarrow C_2H_4^+ + CHO$ [20] $+H+2e$ 15.5 eV.

$(CH_3)_2CO+e \rightarrow C_2H_4^+ + CO + 2H + 2e$ 16.6 eV.

However, a conclusion as to a process suitable for the production of the M/e 28 ion could not be obtained.

**M/e=27** $C_2H_3^+$

This ion must be $C_2H_3^+$. The calculated appearance potentials for this ion are as follows:

$(CH_3)_2CO+e \rightarrow C_2H_3^+$ [19] $+H_2+CHO+2e$ 14.3 eV.

$(CH_3)_2CO+e \rightarrow C_2H_3^+ + H + H_2 + CO + 2e$ 15.5 eV.

$(CH_3)_2CO+e \rightarrow C_2H_3^+ + 3H + CO + 2e$ 19.8 eV.

These values do not agree with the observed value. Therefore, the mechanism of the production of this ion can not be found.

**M/e=15** $CH_3^+$

The calculated appearance potentials of this ion are as follows:

$(CH_3)_2CO+e \rightarrow CH_3^+$ [19] $+CH_3CO$ [20] $+2e$ 13.1 eV.

$(CH_3)_2CO+e \rightarrow CH_3^+ + CH_3 + CO + 2e$ 13.9 eV.

$(CH_3)_2CO+e \rightarrow CH_3^+ + CH + H_2 + CO + 2e$ 16.3 eV.

Accordingly, the second and the third reactions would be possible if the reactions take place with excess energies (kinetic and/or excitational energies) of 1.6 and 1.0 eV. respectively. In order to know the possible reactions conclusively, however, the kinetic energies of produced ions must be measured more precisely.

*4) Ethyl Methyl Ketone*

**M/e=72** $CH_3COC_2H_5^+$

There is a break in the ionization efficiency curve of this ion, and there seem to exist something like breaks above the first break point.

The first ionization potential is thought to be the energy by which the removal of one of the lone pair electrons of the O atom in the molecule takes place, as in the previous discussion of this report. The value obtained by the present author is a little larger than that of acetone. The fact is reasonably explained by assuming that hyper-conjugation is a little smaller in ethyl methyl ketone. This tendency was recognized also in a comparison of dipole moments.

**M/e=57** $C_2H_5CO^+$ or $CH_2CO^+CH_3$

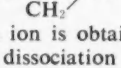
If this ion is assumed to be $C_2H_5CO^+$, the corresponding reaction is as follows:

$$CH_3COC_2H_5 + e \rightarrow C_2H_5CO^+ + CH_3 + 2e$$

Moreover, the structure of the ion produced should be $C_2H_5-C{\equiv}O^+$, which satisfies the trivalency as in the case of $HCO^+$ from formaldehyde and of $CH_3CO^+$ from acetaldehyde as well as acetone. $I(C_2H_5CO)$ is obtained as 7.66 eV. by use of the relations, $A(C_2H_5CO^+) = I(C_2H_5CO) + D(CH_3-COC_2H_5)$ and $D(CH_3-COC_2H_5) = 3.15$ eV[20]. This value is a little smaller than the value of $I(CH_3CO)$ obtained previously in this report.

From the value of $I(C_2H_5CO)$, the stabilization energy by the formation of triple bond of $O^+$ in this ion is calculated as 2.22 eV. (9.88 eV.−7.66 eV.). Hence, the total binding energy of $O^+$ in this ion is obtained as 206 kcal./mol. (157 kcal./mol.[18] + 23.06×2.22 kcal./mol.). This value agrees quite well with the

values for $CH_3C{\equiv}O^+$ obtained in the case of acetaldehyde and acetone.

On the other hand, if this ion is assumed to be  , the ionization potential of this ion is obtained as 7.20 eV., provided that the dissociation energy between C atoms in the ethyl radical in the molecule is assumed as 3.60 eV., which is the dissociation energy of ethane. However, in this case the stabilization due to the formation of the triple bond of $O^+$ in the ion can not take place. The value of 7.20 eV. is therefore thought to be as abnormally small as the ionization of the oxygen atom in the radical.

**M/e=43** $CH_3CO^+$

The assumed reaction for the production of this ion is as follows:

$$CH_3COC_2H_5+e \rightarrow CH_3CO^+ + C_2H_5 + 2e$$

$I(CH_3CO)$ is calculated as 7.97 eV. by the use of $D(CH_3CO-C_2H_5)=3.13$ eV.[20] This value of $I(CH_3CO)$ must, of course, agree with the values of $I(CH_3CO)$ in the cases of acetaldehyde and acetone. In this case also, by assuming 1.91 eV., which is the difference between this value and the ionization potential of the parent molecule, as the stabilization energy due to the formation of the triple bond of $O^+$ in the ion, 202 kcal. is obtained as total bond energy of the $O^+$ in the $CH_3$-$C{\equiv}O^+$ ion (157 kcal.$+23.06\times1.91$ kcal.). This also agrees quite well with the values previously described in this report. Furthermore, the heat of the formation of $CH_3CO^+$ is calculated, by using the value obtained above, as 174 kcal./mol. The value agrees well with the value cited above (cf. Ref. 19).

**M/e=29** $C_2H_5^+$ or $CHO^+$

If this ion is assumed to be $C_2H_5^+$, the heat of reaction, or the appearance potentials, are calculated as follows:

$$CH_3COC_2H_5+e \rightarrow C_2H_5^+ + CH_3CO + 2e \qquad 11.8\text{ eV.}$$

$$CH_3COC_2H_5+e \rightarrow C_2H_5^+ + CH_3 + CO + 2e \qquad 12.55\text{ eV.}$$

The second process seems to take place. In this case, the reaction by which the $CH_3CO$ radical is produced is impossible, as in the case of acetone.

On the other hand, if the ion is assumed to be $CHO^+$, energetically there is some possibility as follows:

$$CH_3COC_2H_5+e \rightarrow CHO^+ + C_3H_7 + 2e \qquad 12.1\text{ eV.}$$

$$CH_3COC_2H_5+e \rightarrow CHO^+ + C_2H_4 + CH_3 + 2e \qquad 13.2\text{ eV.}$$

**M/e=28** $CO^+$ or $C_2H_4^+$

As the appearance ratio of this ion is very small, a high degree of accuracy in measurement can not be expected. The heat of reaction for the following processes is calculated:

$$MeEtCO+e \rightarrow CO^+ + C_3H_8 + 2e \qquad 14.3\text{ eV.}$$

$$MeEtCO+e \rightarrow CO^+ + CH_4 + C_2H_4 + 2e \qquad 16.35\text{ eV.}$$

$$MeEtCO+e \rightarrow CO^+ + Me + Et + 2e \qquad 17.9\text{ eV.}$$

$$MeEtCO+e \rightarrow C_2H_4^+ + CH_4 + CO + 2e \qquad 11.65\text{ eV.}$$

$$MeEtCO+e \rightarrow C_2H_4^+ + CH_3CHO + 2e \qquad 11.8\text{ eV.}$$

$$MeEtCO+e \rightarrow C_2H_4^+ + CH_3 + CHO + 2e \qquad 14.9\text{ eV.}$$

$$MeEtCO+e \rightarrow C_2H_4^+ + CH_2 + H_2 + CO + 2e \qquad 11.6\text{ eV.}$$

If the second appearance potential of 15.6 eV. is rejected for the reason described previously in the discussion on the M/e=28 ion produced from formaldehyde, the first and the third processes will probably be possible.

**M/e=15** $CH_3^+$

The heat of the reaction of the following process is calculated as 15.05 eV.

$$CH_3COC_2H_5+e \rightarrow CH_3^+ + C_2H_5 + CO + 2e$$

The appearance potential of the $CH_3^+$ agrees with the above-calculated heat of reaction if the excess energy of 0.3 eV. is permitted in the above process.

On the other hand, if the reaction is assumed to be $CH_3COC_2H_5+e \rightarrow CH_3^+ + CH_3COCH_2+2e$, and the values of $I(CH_3)$ and $D(C\text{-}C)$ to be 10.0 eV. and 3.6 eV. respectively, the heat of the reaction of this process is obtained as 13.6 eV. This does not agree with the appearance potential.

The reason why the process through which $CH_3^+$ is produced from acetone has a relatively large excess energy, while the process through which $CH_3^+$ is produced from ethyl methyl ketone has a small excess energy, is not obvious.

*5) Heat of Formation of $CHO^+$, $CH_3CO^+$ and $C_2H_5CO^+$*

The appearance potential of an ion is the heat of the reaction by which the ion is formed if no excess energy is involved, and the process may be treated by the usual methods

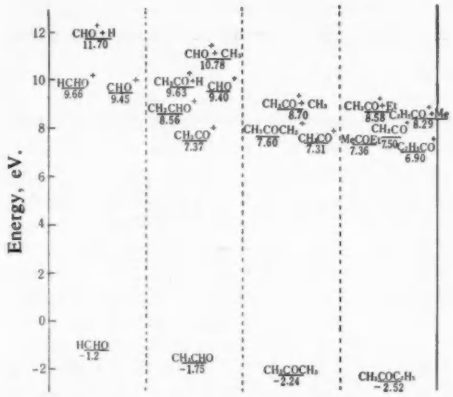



Fig. 2. Heat of formation of ions determined.

of thermochemistry. Thus, for the reaction $R_1R_2 \rightarrow R_1^+ + R_2$, the relation

$$A(R_1^+) = \Delta H_f(R_1^+) + \Delta H_f(R_2) - \Delta H_f(R_1R_2)$$

is given, provided that the reaction involves no excess energy.

By introducing the measured appearance potentials and the heat of formation of related molecules as well as radicals into the above relation, heats of formation of $CHO^+$, $CH_3CO^+$ and $C_2H_5CO^+$ are obtained, as shown in Fig. 2. The agreement between the heats of formation for the same ion produced from different molecules is very good, considering that the values are obtained through the appearance potential study.

## Summary

A study of the ionization and dissociation of formaldehyde, acetaldehyde, acetone and ethyl methyl ketone, all of which have an oxygen atom, was carried out through the appearance potential method. As appearance potentials were obtained by the retarding potential difference method, break points, which correspond to successively occurring ionization, appeared in the ionization efficiency curves of molecules and fragments. By considering the relation of energy, it is concluded that the ionization of the molecule takes place at first by the removal of one of the lone pair electrons of oxygen atom in the molecule, and that, in the formation of a fragment ion including an oxygen atom, dissociation takes place to create a triple bond, satisfying the trivalency of $O^+$ in the fragment ions.

The total bond energy of $O^+$ in $CH_3C{\equiv}O^+$ and $C_2H_5C{\equiv}O^+$ are calculated as about 200 kcal./mol., while in $HC{\equiv}O^+$ it is 170~180 kcal./mol. as in the case of diethyl ether reported previously. This fact may be explained by the number of resonance structures related.

The second and the third ionization potentials are thought to correspond to the removal of the $\pi$-electron and $\sigma$-electron in C–O bond respectively. The heat of formation of $CHO^+$, $CH_3CO^+$ and $C_2H_5CO^+$ are obtained from various reactions.

The author wishes to express his gratitude to Professor K. Kido and Professor T. Titani for their continual guidance and encouragement throughout this work, and to Professor K. Hirota of Osaka University and Professor S. Nagakura of the Institute for Solid State Physics, the University of Tokyo, for their kind advice and valuable discussion. He is also greatly indebted to Mr. Y. Kaneko and Mr. T. Oguri for their earnest co-operation.

*Department of Physics*
*Faculty of Science*
*Tokyo Metropolitan University*
*Setagaya-ku, Tokyo*

## SHORT COMMUNICATIONS

### *The Polymerization of γ-Methyl-L-glutamate-N-carboxyanhydride Initiated with Acetic Acid*

By Tôru OKUDA and Setsuji SAKURAI

(Received August 26, 1961)

The rate of polymerization of *N*-carboxyanhydrides (NCAs) of α-amino acids and the molecular weight of polypeptides formed vary widely with the characteristic of reaction medium and initiator[1-3]. We have found that for the polymerization of γ-methyl-L-glutamate-NCA, acetic acid which has little or no initiating ability in one solvent, does act as an initiator in another solvent. Thus, when the NCA was dissolved in chloroform ($1.07\times10^{-1}$ mol. $l^{-1}$) containing acetic acid ($5.35\times10^{-2}$ mol. $l^{-1}$), rapid polymerization occurred, and completed within 130 min., while in dioxane solution no appreciable reaction was observed. Addition of dioxane (10% by volume) to the chloroform solution of the NCA caused an induction period of approximate 70 min. and a depression in rate (See Fig. 1). The evolution of carbon dioxide upon dissolution of the NCA in acetic acid was much slower than in the system chloroform-acetic acid. From the reaction mixture in acetic acid we were able to isolate only terminal-free low molecular weight peptide, which, according to the results of elementary analysis and optical rotation in dichloroacetic acid, had no acetyl group and was composed of 3 units of γ-methyl-L-glutamate residue. Found: C, 47.1; H, 6.71; N, 9.53. Calcd. for $(C_6H_9O_3N)_3\cdot H_2O$: C, 48.3; H, 6.49; N, 9.40%. $[\alpha]_D^{23}=17°$ (*c* 1.9). So far, no other products such as acetylated derivatives, diketopiperazine or cyclic peptide have been detected.

The fact that the degree of polymerization of the final polymer obtained in the polymerization in chloroform is much higher ($[\eta]=0.98$, $\overline{DP}=500\sim600$) than that expected from the initial NCA-initiator ratio of 2 indicates that only a small part of acetic acid was utilized as a true initiator. Therefore, the behavior of acetic acid as an initiator in chloroform solution seems to resemble somewhat that of tertiary amine.

Fig. 2 shows that two successive propagation rates exist. Similar change in propagation rate was observed in polymerizations of other NCAs[3-8] and explained either by conformational change (random or β-form to α-helix)

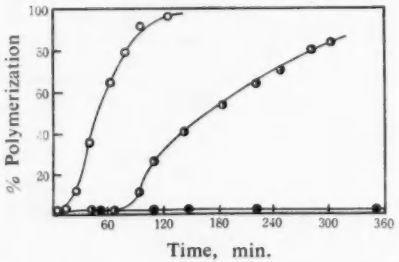



Fig. 1. Time-conversion curves for polymerization of γ-methyl-L-glutamate-NCA ($1.07\times10^{-1}$ mol. $l^{-1}$) indicated with acetic acid ($5.35\times10^{-2}$ mol. $l^{-1}$) in solution at 30°C.
—○—: In chloroform, —◑—: in chloroform-dioxane (9:1 by volume), —●—: in dioxane.

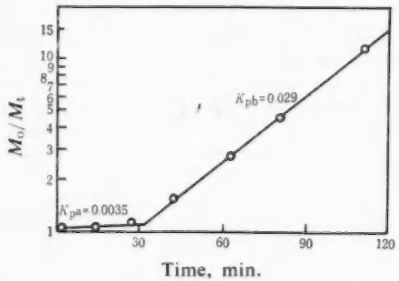



Fig. 2. The polymerization of γ-methyl-L-glutamate-NCA in chloroform at 30°C, initiated with acetic acid under the condition given in Fig. 1. The values of [NCA] initially and at time *t* are denoted by $M_0$ and $M_t$, respectively.

1) E. R. Blout and R. H. Karlson, *J. Am. Chem. Soc.*, **78**, 941 (1956).
2) C. H. Bamford, A. Elliott and W. E. Hanby, "Synthetic polypeptides", Academic Press Inc., New York, N. Y. (1956), p. 92.
3) R. D. Lundberg and P. Doty, *J. Am. Chem. Soc.*, **79**, 3961 (1957).
4) P. Doty and R. D. Lundberg, ibid., **78**, 4810 (1956).
5) T. Okuda, A. Akamatsu and Y. Takeda, unpublished data.
6) D. G. H. Ballard and C. H. Bamford, *J. Chem. Soc.*, **1959**, 1039.
7) H. Weingarten, *J. Am. Chem. Soc.*, **80**, 352 (1958).
8) J. D. Coombes and E. Katchalaski, ibid., **82**, 5280 (1960).

in the growing polypeptide chain[4,7], or by gel effect due to precipitation of polymer or gelation[6]. In the present case, after a slow propagation rate, when about one-tenth of the NCA had been consumed the propagation shifted to a faster rate. Since the average DP of the polymer was found to be 500~600, the transition occurred when the growing polypeptide chain had reached a $\overline{DP}=50\sim60$. Because this value exceeds the one necessary for the conformational transition of poly-γ-methyl-L-glutamate (15~25 residues[5]) the gel effect might be more responsible for occurrence of the two successive propagation rates.

We wish to express our thanks to Drs. H. Oeda and T. Yoshida for permission to publish the present work.

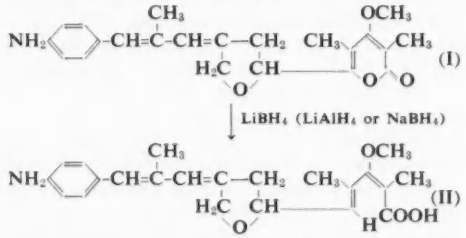
*Central Research Laboratory*
*Ajinomoto Co., Inc.*
*Kawasaki*

## *Reduction of α-Pyrones with Complex Metal Hydrides*

By Kiyoyuki YAMADA, Mitsuo ISHIZAKA and Yoshimasa HIRATA

(Received November 21, 1961)

During the course of the structural investigation of aureothin[1], we obtained several derivatives that were regarded as products of unusual reactions. One of the remarkable examples is "aminol H" (II) which was produced from isoaureothamine (I) by treatment with various complex metal hydrides[2].




In order to examine whether or not the occurrence of this rather unexpected reduction is due to the complexity of the other part of the molecule, reduction of simple α-pyrones with complex metal hydrides was carried out.

4, 6-Dimethyl-α-pyrone, when treated with lithium aluminum hydride in tetrahydrofuran, gave β-methylsorbic acid, m. p. 97°C[3] (Found: C, 67.00; H, 8.10. Calcd. for $C_7H_{10}O_2$: C, 66.46; H, 7.99%. Ultraviolet spectrum, $\lambda_{max}^{EtOH}$, 260 mμ, log ε, 4.0). Reduction of 4, 6-dimethyl-α-pyrone with lithium borohydride in a similar condition also gave the same acid, whereas no reaction took place with sodium borohydride.

Further, lithium aluminum hydride reduction of 4-methoxy-6-methyl-α-pyrone, which is a good model compound for isoaureothamine (I), yielded β-methoxysorbic acid (III) (m. p. 147~149°C (decomp.)[4]. Found: C, 59.17; H, 7.13. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09%. Ultraviolet spectrum, $\lambda_{max}^{EtOH}$, 264 mμ, log ε, 4.1) and a neutral product (b. p. 101~104°C/16 mmHg. One methoxyl group. Ultraviolet spectrum; $\lambda_{max}^{EtOH}$, 239 mμ) which was shown to be identical with 3-methoxy-2, 4-hexadienol (IV) obtained from β-methoxysorbic acid by lithium aluminum hydride reduction.

The relative amounts of the two products, III and IV, are considerably dependent on the reaction conditions (temperature, manner of addition, etc.), the details of which will be reported elsewhere. Thus, it was established that generally the hydrogenolysis of the 1, 6-linkage of the α-pyrone ring occurs in the reduction using complex metal hydrides.

*Chemical Institute*
*Faculty of Science*
*Nagoya University*
*Chikusa-ku, Nagoya*

1) K. Yamada, H. Nakata and Y. Hirata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 340 (1960).
2) K. Yamada, T. Naito, K. Okuhara, H. Nakata and Y. Hirata, This Bulletin, **33**, 1303 (1960).
3) H. Burton and C. K. Ingold, *J. Chem. Soc.*, **1929**, 2022; R. Kuhn and M. Hoffer, *Ber.*, **65**, 651 (1932).
4) E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, **1949**, 1423; H. B. Henbest and E. R. H. Jones, ibid., **1950**, 3628.

## *Mechanisms of the Wallach Rearrangement*

By Shigeru OAE, Tsugio FUKUMOTO and Masayuki YAMAGAMI

(Received October 23, 1961)

Shemyakin, Maimind and Vaichunaite[1] have shown, using $^{15}N$-labeled azoxybenzene (I) that I was observed to rearrange to 4-hydroxyazobenzene (III) or (IV) under various conditions[2,3]

1) M. M. Shemyakin, V. J. Maimind and B. K. Vaichunaite, *Chem. & Ind.*, **1958**, 755; Izvestia Akad. *Nauk S. S. S. R., Otdel. Khim. Nauk*, 866 (1960).
2) P. H. Gore and G. K. Hughes, *Austral. J. Sci. Research*, **3A**, 136 (1950); *Chem. Abstr.*, **45**, 2889 (1951).
3) V. O. Lukashwish and T. N. Khurdyumova, *Zhur. Obshchei Khim.*, **18**, 1961 (1948).

in which the two benzene rings were attacked with equal ease. Azoxybenzene recovered from these reactions remained practically unchanged in isotope distribution: They postulated that the rearrangement proceeds through a symmetrical intermediate, II.

$$C_6H_5\text{-}N(O)=^{15}N\text{-}C_6H_5 \xrightarrow{H_2SO_4} \left[C_6H_5\text{-}N\text{-}^{15}N\text{-}C_6H_5 \;(O)\right]$$

I II

$$\longrightarrow C_6H_5\text{-}N=^{15}N\text{-}C_6H_4OH(p)$$

III

$$C_6H_5\text{-}^{15}N=N\text{-}C_6H_4OH(p)$$

IV

The formation of the *N, N*-oxide intermediate II was further emphasized by the Russian workers[4] in their finding that there was no incorporation of $^{18}O$ into *p*-nitroazoxybenzene from $^{18}O$-labeled sulfuric acid in the isomerization of *β-p*-nitroazoxybenzene (V) to *α-p*-nitroazoxybenzene (VI).

$$C_6H_5\text{-}N=N\text{-}C_6H_4NO_2(p) \rightarrow C_6H_5\text{-}N=N\text{-}C_6H_4NO_2(p)$$

(O) (O)

V VI

An alternative mechanism was suggested by Gore[5] to proceed via monocation (VII) in which nucleophilic attack by $-OSO_2OH$ or $-OSO_2Cl$ is restricted to the far ring.

$$C_6H_5\text{-}\overset{\oplus}{N}(OH)=N\text{-}C_6H_5 \leftrightarrow C_6H_5\text{-}N\text{-}N=\langle\!\rangle\!\rangle^{\oplus}$$

OH

VII

The latter mechanism is similar to that of the Bamberger reaction[6] and one can expect that the *p*-positions would be attacked preferentially by more nucleophilic ethoxy group when the reaction is conducted in the mixture of ethanol-sulfuric acid as was shown by Yukawa[7], in the case of the Bamberger reaction. *p*-Aminophenol formed by the Bamberger reaction of phenylhydroxylamine was shown to incorporate $^{18}O$ from the reaction medium when the reaction was carried out in $^{18}O$-labeled sulfuric acid[8]. We have carried out the reaction by heating azoxybenzene in the mixture of ethanol and sulfuric acid for 5 hr. at 90°C, but the reaction was found to proceed very little, recovering original material in almost quantitative yield. We have reacted azoxybenzene in 83% sulfuric acid, labeled by 0.67% $^{18}O$ and found that the resulting *p*-hydroxyazobenzene incorporated no $^{18}O$ from the medium ($CO_2$ found, 0.202 $^{18}O$, tank $CO_2$, 0.204% $^{18}O$). We also found that the rearrangement of *α-p*-bromoazoxybenzene was much slower than that of unsubstituted compound in the same medium (83% $H_2SO_4$).

$$C_6H_5\text{-}N=N\text{-}C_6H_4Br(p) \rightarrow HOC_6H_4\text{-}N=N\text{-}C_6H_4Br(p)$$

(O)

VIII IX

*α-p*-Nitroazoxybenzene is known to rearrange slowly[5]. These findings together with the fact that a substantial proportion of azoxybenzene is reduced by potassium iodide to azobenzene in the rearrangement reaction in chlorosulfonic acid, seem to suggest that the rearrangement in these oxy-acids is an acid catalyzed bimolecular oxidation reaction where *p*-positions of benzene rings of the *N, N*-oxide II or of azoxybenzene are attacked by oxygen of protonated *N, N*-oxide II or *N*-oxide.

A similar rearrangement of azoxybenzene to *o*-hydroxyazobenzene by ultraviolet light has been known[9]. In this case, the reaction take place not only in non-acidic medium, such as aqueous alcohol but also in solid state. The Russian workers[1] found that the original excess of $^{15}N$ was in the nitrogen group attached to the hydroxylated benzene when carried out the reaction in 85% ethanol for 65 hr. at 30~45°C. We have carried out the reaction in 85% ethanol containing 15% $H_2{}^{18}O$ (enriched by 0.67% $^{18}O$) and found that the resulting *o*-hydroxyazobenzene incorporated very little excess $^{18}O$ from the medium ($CO_2$ found, 0.213% of $^{18}O$, tank $CO_2$, 0.204% $^{18}O$). We favor that the reaction proceeds through an intramolecular oxygen radical shift from *N*-oxide. A similar free radical shift is known in the reaction of dimethylaniline-*N*-oxide with acetic anhydride[10].

Further work is in progress in this laboratory to elucidate the mechanism using $^{18}O$-labeled azoxybenzene. Details of this work and further work will be published shortly.

*Department of Chemistry*
*Radiation Center of Osaka Prefecture*
*Sakai, Osaka*

4) M. M. Shemyakin, V. J. Maimind and Ts. E. Agadzhanyan, *Chem. & Ind.*, **1961**, 1223.
5) P. H. Gore, ibid., **1959**, 191.
6) a) "Name Reactions in Organic Chemistry" (Jinmei Yuki-Hanno-Shu), Vol. II, Ed. by M. Murakami and Y. Yukawa, Asakura Book Co. (1954), p. 228.
b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell Univ. Press (1953), p. 621.
7) Y. Yukawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **71**, 603 (1950).
8) S. Okazaki and M. Okumura, unpublished work,—private communication.
9) a) W. M. Cumming and G. S. Ferrier, *J. Chem. Soc.*, **127**, 2374 (1925).
b) G. M. Badger and R. G. Buttery, ibid., **1954**, 2243.
10) S. Oae, T. Kitao and Y. Kitaoka, 12th. Mechanism Conference Reports, the Chemical Society of Japan, Sendai, October, 1961.

## Additions and Corrections

Volume 33, 1960

Y. Kubokawa: Chemisorption of Hydrogen on Zinc Oxide. I and II.

Page 550. In col. 2, line 9, for "10~31" read "10 to 31".

Page 551. In Fig. 3, ordinate, for "0.0" read "0.10".

Page 554. In col. 2, line 22 from the bottom, insert "of desorption" in front of "corresponding".

Y. Kubokawa: Carbon Monoxide Chemisorption on Zinc Oxide.

Page 557. In col. 1, line 23, for "2.5 kcal./mol." read "12.5 kcal./mol."; In col. 2, line 9, for "some" read "same".

Page 558. In Fig. 8, ordinate, for "1.5" read "$\bar{1}.5$".

Page 559. In Fig. 10, ordinate, for "3.5, 3.0 and 4.5" read "$\bar{3}.5$, $\bar{3}.0$ and $\bar{4}.5$".

Y. Kubokawa: An Interpretation of the Elovich Equation for the Rate of Chemisorption on the Basis of Surface Heterogeneity.

Page 734. In col. 2, Eq. 2, for "$\nu$" read "$v$".

S. Morosawa: Studies on Seven-Membered Heterocyclic Compounds Containing Nitrogen. IV and V.

Page 1110. In col. 1, lines 8-10, delete ", together with that of the condensation product of XIV ethiodide with *p*-dimethylaminobenzaldehyde".

Page 1111. In col. 2, line 31, for "67.5%" read "6.75%"; line 15 from the bottom, for "5 (or 6)-Ethoxycarbonyl-1,2,5(or 1,2,6)-triazazulene" read "5(or 6)-Ethoxycarbonyl-hexahydro-1,2,5(or 1,2,6)-triazazulene".

Page 1112. In col. 1, first line, for "$C_{10}H_{15}N_2O_3$" read "$C_{10}H_{15}O_2N_3$".

Page 1113. Formula III should have one more double bond in the ring.

Page 1114. In col. 2, line 5, for "-tetrahydroheptiadole" read "-tetrahydroheptindole".

K. Hiromi: Theory of the Influence of the Dielectric Constant on the Rate of Reaction in Solution with Application to Enzyme Reactions. I and II.

Page 1253. In Eq. 9, for "$\sum_{k=1}^{M}\sum_{l\neq k}$" read "$\sum_{k=1}^{M}\sum_{l\neq k}$".

Page 1254. In col. 2, line 5 from the bottom, for "$e_1$ anp $e_3$" read "$e_1$ and $e_3$".

Page 1257. In Table IV, for "$\frac{\mathrm{d}\log k_1}{\mathrm{d}(1/D)}$" read "$\frac{\mathrm{d}\log k_1}{\mathrm{d}(1/D)}$[21]".

Page 1258. In Table V, for "$\frac{\mathrm{d}\log k}{\mathrm{d}(1/D)}$" read "$\frac{\mathrm{d}\log k}{\mathrm{d}(1/D)}$[6]".

Page 1259. In col. 1, line 12 from the bottom, for "treatmnets" read "treatments", line 3 from the bottom, for "Laidler-Lands-kroener's" read "Laidler-Landskroener's".

Page 1265. In Eq. 4, the last term, for "$\sum_{i=1}^{n}$" read "$\sum_{s=1}^{n}$".

Page 1267. In Table I, col. 5, lines 1, 2 and 3 from the bottom, for all the "$k_4$" read "$k_d$".

H. Onishi and N. Ishiwatari: Spectrophotometric Determination of Bismuth with Xylenol Orange.

Page 1583. In Fig. 6, for "0.50 $\mu$mole Bi" read "0.55 $\mu$mole Bi".

Page 1584. In col. 1, line 3 from the bottom, for "$1\times10^7$" read "$3.3\times10^5$", last line, delete "This value is greater than that of the iron(III)-Xylenol Orange complex ($5\times10^5$)[4], and is close to that of the zirconium-Xylenol Orange complex ($4.0\times10^7$)[8]".

S. Kuwata: Studies on Pelletierine. I and II.

Page 1668. In footnote 6), for "*Koincl.*" read "*Koinkl.*".

Page 1672. By Shigeru Kuwata (printed erroneously as Sigeru Kuwata).

Page 1673. In Table I, for "RHOSPHORUS PENTOXIDE" read "PHOSPHORUS PENTACHLORIDE"; In col. 2, Formula IV, the bond should be replaced.

Page 1675. In col. 1, last line, for "m. p·" read "m. p."; In col. 2, line 15 from the bottom, for "conflct" read "conflict"; In footnote 7), for "*Koincl.*" read "*Koinkl.*".

H. Nakata: Correlation of Reaction Rates and Product Stabilities. I and II.

Entirely through the author's fault, the texts of these articles as appeared in This Bulletin, **33**, 1688 and 1693 (1960), were not seen in proof by the author before printing, and hence contain a number of errors which are corrected herein. The author offers his sincere apology for the readers.

Page 1689. In col. 1, the formula IV should have one more double bond in the benzene ring. In the formula V, "$H_3C$" in the tetrahydrofuran ring should be "$H_2C$". In the formula VI, "$CH_3$" should be added to the oxygen at the top of the pyronone ring to give a methoxyl group. In col. 1, line 21, delete a comma after "indicates". In line 23, insert "in" after

"predominates". In footnote 5), line 2, "ibid., 374 (1958)" should be "ibid., **79**, 374 (1958)." In col. 2, line 24, delete a comma after "reaction".

Page 1690. In col. 2, under the formula VIII$\gamma$, for "6M-ethyl-" read "6-Methyl-". In footnote 42), line 1, delete a comma after "observed".

Page 1691. In col. 1, line 24, delete a comma after "suggest". In line 24, for "either" read "ether". In col. 2, footnote 52), lines 3—4, delete "is" after "tautomer".

Page 1694. In col. 2, the formula IV, "$C_1$" should be "$O_1$".

Page 1695. In col. 1, line 24, delete "is".

Page 1696. In col. 2, line 18, delete a comma after "accurately",

Page 1697. In col. 1, line 19, insert "in the" after "percentage". In the formula VII$\gamma$, delete "H" on the carbonyl oxygen. In the formula VIII$\gamma$, the double bond should be replaced.

Page 1698. In col. 2, lines 12—13, for "*electronic delocalization*" read "*electron distribution*". In line 21, for "electronic delocalization" read "electron distribution". In line 23, for "electronic delocalization" read "electron distribution".

S. Yamana: Molecular Rotations of Polyhydroxycyclohexanes in Relation to their Structures.

Page 1741. In footnote 3), line 4 from the bottom, for "$=\sum[\mu]^{20}_{D\,obs}$" read "$\equiv\sum[\mu]^{20}_{D\,obs}$".

Page 1742. In col. 2, line 11 from the bottom, for "$\sum[\mu]_{obs}$" read "$\sum[\mu]^{20}_{D\,obs}$".

## Additions and Corrections

Volume 34, 1961

Y. Sato, T. Meshi and T. Takahashi: Studies on Tritium Labeled Compounds. II.

Page 168. In col. 2, line 8, for "$A=\sigma Nf(1-e^{-0.693/t})$" read "$A=\sigma Nf(1-e^{-0.693t/T})$".

M. Kinoshita and S. Umezawa: Studies on Antibiotics and Related Substances. XII.

Page 312. In col. 2, line 11, for "7.8 mg./ml." read "7.8 mcg./ml.".

A. Sugimori: The Competitive Reduction of Nitrobenzene and para-Substituted Nitrobenzenes with Nickel Catalysts.

Pages 407—411. For all "mM"s read "mmol."s.

A. Sugimori and G. Tsuchihashi: Radiolysis of Crystalline Oxalato Complexes.

Page 450. In col. 1, line 17 from the bottom, insert "per 100 eV. of absorbed energy" in front of ")"; line 15 from the bottom, insert "per 100 eV. of absorbed energy" in front of ")"; line 14 from the bottom, insert "(the number of the decomposed oxalate ions per 100 eV. of absorbed energy)" in front of "are".

Y. Katsube, K. Uesugi and J. H. Yoe: Spectrophotometric Determination of Nitrite in Nitrate and Sulfate.

Page 743. In Table I, for "5000 mg. $SO_4^{2-}$/25 ml." read "1500 mg. $SO_4^{2-}$/25 ml.".

Y. Katsube, K. Uesugi and J. H. Yoe: Spectrophotometric Determination of Uranium with Sodium 2'',6''-dichloro-4'-hydroxy-3,3'-dimethylfuchsone-5,5'-dicarboxylate.

Page 827. The axis of ordinate of Fig. 3, for "Absorbance at 610 m$\mu$" read "Absorbance at 640 m$\mu$".

Y. Yoshino, Y. Tsunoda and A. Ouchi: Manganese(III) Complexes Ethylenediaminetetraacetic Acid.

Page 1195. In Fig. 2, for "$9.34\times10^{-4}$ mol./l." read "$1.40\times10^{-3}$ mol./l.".

S. Yamana: Molecular Rotations of Polyhydroxycyclohexanes in Relation to their Structures. II.

Page 1213. In col. 1, line 15, for "$[M]^{19}_{D}$(W)" read "$[M]^{20}_{D}$(W)".

S. Yamana: Molecular Rotations of Terpenes in Relation to their Structures. I.

Page 1414. In footnote 2), line 1, for "$C^{\alpha s}$-Atom" read "$C^{\alpha s}$-atom".

Page 1415. In footnote 10), for "Zeitshel" read "Zeitschel"; In footnote 18), line 3 from the bottom, for "$\partial/\partial n\{(n^2+2)/\}3\partial n$" read "$\partial/\partial n\{(n^2+2)/3\}\partial n$".

Page 1416. In col. 2, line 14 from the bottom, for "$\zeta_{CH}\zeta_{OH}$" read "$\zeta_{CH_3}\zeta_{OH}$".

Page 1417. In Eq. 6, line 2, delete "$\equiv$", substitute "$=$" before the parenthesis; In col. 1, line 7 from the bottom, add "in" after "$\zeta'_{OH^2}$".

Page 1418. In col. 1, line 6 from the bottom, for "to" read "do".

# AUTHOR INDEX TO VOLUME 34, 1961


ABE, M. See ITO, T., 1736.
ABE, T. Absorption Spectra of Unstable Colored Intermediates from Picryl Chloride by the Action of Sodium Hydroxide ..... 21
ABE, T. Visible Absorption Spectra of 1,3,5-Trinitrobenzene and its Derivatives in Aqueous Alkaline Acetone .....1776
AKABORI, S. Protection of Amide-Nitrogen for Peptide Synthesis. A Novel Synthesis of Peptides Containing *C*-Terminal Glutamine ..... 739
AKABORI, S. See AKAMATSU, A., 1067, 1302.
AKAISHI, J. The Preparation of Carrier-free $^{234}$Th(UX) by Anion Exchange from Nitric Acid-Alcohol Mixed Solution of Uranyl Nitrate .....1198
AKAMATSU, A. Studies on the Silk-platinum Catalyst. I.....1067
II .....1302
AKAMATU, H. See INOKUCHI, H., 749, 1093.
AKAMATU, H. See UCHIDA, T., 1015.
AKAMATU, H. See SANO, M., 1569.
AKIYOSHI, S. See KOBAYASHI, H., 1123.
ALI, S. I. See MALIK, W. U., 1306. 1310.
AMANO, H. See BABA, H., 590.
AMAYA, K. Thermodynamical Studies on Binary Systems Consisting of Polar and Non-polar Liquids. I .....1271
II .....1278
III .....1349
IV .....1584
V .....1592
AMAYA, K. Statistical Thermodynamics of Solutions of Optically Active Substances. I...1689
II .....1803
AMAYA, K. Liquid-Vapor Equilibrium of Isotope Mixture under Centrifugal Force.....1807
AMEMIYA, A. See HIRANO, Y., 292.
AMIYA, T. See SUZUKI, A., 455.
AMIYA, T. The Aconite Alkaloids. XXXV..... 898
ANDO, J. Mineral Content of Mixed Fertillizer ..... 678
AOKI, J. Studies of Violanthrone B. I.....1817
II .....1820
ARAI, A. Syntheses of γ-Ionone Analogues. I-II .....1571
ARAKAWA, H. See NAKAZAKI, M., 453. 1246.
ARAKAWA, K. Rheological Properties of Hydrogels of Agar-agar .....1233
ARAKAWA, K. Stress Relaxation of Gels of Polyvinyl Alcohol-Glycerin-Water System.....1549
ARAKI, C. See HIRASE, S., 1048.
ASAHI, Y. Polarography of Narcotine-*N*-oxide .....1185
ASAO, T. See NOZOE, T., 146.
ASAO, T. On Pyrazino [d, d'] ditropone and its Derivatives..... 151
ASANO, T. See KITAHARA, Y., 589.
ASHIKARI, N. Polymerization of Propylene with Tin Tetraalkyl-Titanium Tetrachloride Catalysts ..... 767
BABA, H. Electronic Spectra of Substituted Aromatic Hydrocarbons. I ..... 76
II ..... 82
BABA, H. Thermal Annealing of Recoil Atoms in Neutron Irradiation of Inorganic Phosphorus Compounds ..... 590
CHITOKU, K. Dielectric Investigation on Coals. V ..... 320
DEGUCHI, Y. Electron Paramagnetic Resonance Study of Diphenyl Nitric Oxide in Single Crystals ..... 910
DESHMUKH, G. S. Polarographic Behavior of Vanadium and Iron in Thiocyanate ..... 325
DOI, K. Preparation of 4-Aminotropolones by Amination of 3-Iodotropolones with Alkali Amides in Liquid Ammonia ..... 497
DOI, K. The Schmidt Reaction in Some Tropolone Derivatives..... 501
DOI, K. Partial Debromination of Polybromotropolones with Cuprous Cyanide and Some Reactions of 4-Bromotropolone..... 504
DOI, K. See NOZOE, T., 312. 611. 614.
DOI, K. Some Electrophilic Substitution Reactions of 4-Aminotropolone .....1410
EBIHARA, H. See IKEDA, N., 1705.
EBINE, S. Anionoid Substitution of Bromo-3, 4-benzotropolones ..... 887
ENDO, K. See KIGOSHI, K., 1739.
FUJII, T. See NAKAGAKI, M., 433.
FUJIMOTO, M. A Novel Resin Spot Test for Copper(II) Using a Chelating Resin .....1342
FUJIMOTO, M. Zur einfachen Bestimmung in Wasser Milliardestelmenge vorhandenen Kupfers(II) durch Anreicherung mit Mikroschicht der Chelatbildungsharze .....1537
FUJIMURA, T. See KŌSHIRO, T., 476.
FUJINO, M. Steric Configuration of the α, β-Diaminobutyric Acid Isolated from the Antibiotic Glumamycin ..... 740
FUJISAWA, T. See MUKAIYAMA, T., 812.
FUJISHIRO, R. See KIMURA, K., 304.
FUJITA, K. Oxidation of Terpene Compounds with *tert*-Butyl Chromate. VII ..... 968
FUJIWARA, M. See HAGIHARA, N., 892.
FUJIWARA, S. See NAKAGAWA, N., 143.
FUJIWARA, S. Nuclear Magnetic Resonance of Tar Products. II ..... 881
FUKADA, N. Syntheses of Two Kinds of Metal-free Tetra-azaporphines by the Urea-melt Method ..... 884
FUKUDA, N. On the Constitution of Sulfo-Aluminous Clinker ..... 138
FUKUI, K. Molecular Orbital Theory of Reactivity in Non-Alternant Hydrocarbons ..... 37
FUKUI, K. Theoretical Reactivity Index of Addition in the "Frontier Electron Theory" ..... 230
FUKUI, K. "Frontier Electron Density" in Saturated Hydrocarbons ..... 442

FUKUI, K. See YONEZAWA, T., 707. 747.
FUKUI, K. A LCUAO Treatment of Reactivity in Aromatic Hydrocarbons..... 712
FUKUI, K. A Molecular Orbital Treatment of Triallyl Isocyanurates and Related Allyl Esters ..... 851
FUKUI, K. A Simple Reactivity Index for Alternant Hydrocarbons ..... 933
FUKUI, K. A Theoretical Treatment of Molecular Complexes. I .....1076
FUKUI, K. A New Quantum-mechanical Reactivity Index for Saturated Compounds .....1111
FUKUI, K. An Attempt to Discuss Reactivities of Excited Molecules by the Molecular Orbital Method .....1178
FUKUI, K. Electronic Structure and Biochemical Activities in Diethyl Phenyl Phosphates .....1224
FUKUMOTO, T. See OAE, S., 1873.
FUNAKUBO, E. See MITSUTOMI, A., 1698.
FURUDATE, K. See MATUURA, R., 395.
GAMO, I. Infrared Spectra of Water of Crystallization in Some Inorganic Chlorides and Sulfates ..... 760
GAMO, I. Infrared Absorption Spectra of Water of Crystallization in Copper Sulfate Penta- and Monohydrate Crystals..... 764
GAMO, I. Infrared Absorption Spectra of Water of Crystallization in Cobaltous Chloride Hexa- and Dihydrate Crystals .....1430
GAMO, I. Infrared Absorption Spectra of Water of Crystallization in Ferrous Chloride Tetrahydrate Crystals.....1433
GONDA, K. See OHTAKI, H., 293.
GOTO, R. Studies on the Chemical Decomposition of Simple Sugars. X ..... 753
HAGIHARA, N. See NAKAMURA, A., 452.
HAGIHARA, N. Catalytic Dimerization of Monoalkyl Acetylenes..... 892
HAMADA, K. Kinetics of the Reduction of Selenious Acid by Sulfur Dioxide. I..... 593
II ..... 596
III ..... 600
HAMAGUCHI, H. See KAWASHIMA, T., 701.
HAMANAKA, I. See UNO, T., 1448.
HARADA, K. See KANEKO, T., 1314.
HARADA, Y. On the Optical Absorption Spectra of Semiquinone Ions..... 585
HASHIMOTO, M. Studies on Meso-ionic Compounds. XIII ..... 668
HATA, N. Photochemical Processes due to $n$-$\pi$ and $\pi$-$\pi$ Transitions of 2-Picoline *N*-Oxide in the Vapor Phase.....1440
HATA, N. Photochemical Processes due to $n$-$\pi$ and $\pi$-$\pi$ Transitions of 3-Picoline *N*-Oxide in the Vapor Phase.....1444
HATA, T. See MUKAIYAMA, T., 99.
HATADA, K. See MURAHASHI, S., 631. 939.
HATADA, M. See HIROTA, K., 226. 1644.
HATTORI, S. See YONEZAWA, T., 707.
HAYAKAWA, T. See SUGIURA, T., 58.
HAYAMI, J. See GOTO, R., 753.
HAYAMI, J. Studies on the Chemical Decomposition of Simple Sugars. XI..... 924
XII ..... 927
HAYASHI, J. See ODANI, H., 817.
HAYASHI, K. See SATOH, T., 1260.
HAYASHI, M. Interactions of Surface Active Agents with Congo Red ..... 119
HAYASHI, T. Studies on the Diacylaminoanthraquinone Dyes .....1116
HAZATO, G. See TAKAHASHI, K., 1599.
HIGASI, K. See CHITOKU, K., 320.
HIGUCHI, I. Experimental Evidence for the Theoretical Condensation Isotherm on Spheres Arranged in the Closest Packing.....1539
HIIRO, K. A New Method for the Determination of Boron by Spectrophotometry with Pyrocatecholviolet .....1743
HIIRO, K. A New Method for the Spectrophotometric Determination of Boron with Quercetin .....1748
HIRANO, Y. Selectivity in Radiation-Induced Crosslinking and Scission of Polyvinyl Alcohol (PVA) ..... 292
HIRASE, S. Isolation of 6-*O*-Methyl-D-galactose from the Agar of Ceramium Boydenii .....1048
HIRATA, Y. See OKUMURA, Y., 895.
HIRATA, Y. See YAMADA, K., 1873.
HIROTA, E. See WADA, K., 337.
HIROTA, E. Microwave Spectrum of Propargyl Halides. I ..... 341
HIROTA, E. See KIKUCHI, Y., 348.
HIROTA, K. Studies on Mass Spectra and Appearance Potentials of Acetic Acid and Deuteroacetic Acid $CD_3$ COOH ..... 226
HIROTA, K. See KUWATA, K., 291. 458.
HIROTA, K. Studies on Surface Heterogeneity in Adsorption of Carbon Dioxide on Nickel by Use of the Isotopic Desorption Method.....1213
HIROTA, K. The Polymerization of Vinyl Acetate Catalyzed by Iodine .....1340
HIROTA, K. Synthesis of Several Tertiary Alcohols from Propanol-2 and Ethylene by Gamma-ray Irradiation.....1644
HIROTA, M. See ŌKI, M., 374. 378.
HISANO, T. See MATSUDA, R., 649.
HONDA, K. Simultaneous Polarographic Determination of a System of *o*-Nitroanisole, *o*-Chloronitrobenzene and *o*-Nitrophenol ..... 529
HONDA, M. See ASHIKARI, N., 767.
HORI, K. See MORI, M., 1809.
HORI, R. See SHINODA, K., 237.
HORIE, T. Sudachitin, a New Flavone Pigment of Sudachi .....1547
HOSOYA, H. See ŌKI, M., 1391.
HOSOYA, T. See KURAISHI, M., 780, 1101.
HOTTA, H. Oxidation of Ferrous Ions in Aqueous Solutions by Cobalt-60 Gamma Rays. II .....1640
ICHIBA, S. See YAJIMA, S., 133. 493. 697.
ICHIKAWA, F. A Study on Anion Exchange and Amine Extraction of Rare Earth Elements in Nitric Acid ..... 183
ICHIKAWA, F. Distribution of Various Elements between Nitric Acid and Anion Exchange Resin ..... 952
ICHIKIZAKI, I. See ARAI, A., 1571.
ICHIKUNI, M. Sur la Dissolution des Minerais Sulfurés en Divers Milieux. V .....1780
ICHINOKAWA, H. See KURAISHI, M., 780. 1101.
IGARASHI, M. Molecular Structure of Epibromohydrin and Glycidol by Electron Diffraction ..... 365

IGARASHI, M. An Electron Diffraction Investigation of the Molecular Structure of Ethylenimine ..... 369
IGARASHI, M. See YAMAHA, M., 733.
IGARASHI, M. See KAWAI, T., 1472.
IGARASHI, M. Syntheses of α-Keto Amides and Acids from Ethyl Alkylidenecyanoacetate.....1543
IIKUBO, Y. See IMOTO, K., 186.
IKEDA, M. See ISHIKAWA, T., 1329.
IKEDA, N. Mechanism of the Recoil Phenomena in Hexamminecobalt(III) Chloride ..... 140
IKEDA, N. Hot-atom Chemistry of Hexamminechromium(III) Nitrate in the Solid State.....1705
IKEDA, S. On the Differences in Monolayer Properties of Poly-γ-benzyl-L-glutamate and Poly-β-benzyl-L-aspartate..... 416
IKEDA, S. Monolayer Studies on Polyanhydro-L-glutamic and Polyanhydro-L-aspartic Acids ..... 422
IKEDA, S. See ISEMURA, T., 1236.
IKEGAMI, Y. Infrared Spectra of Troponoids Compounds. II ..... 91
III ..... 94
IMAI, H. See SHINAGAWA, M., 445.
IMAI, H. See ICHIKAWA, F., 952.
IMAI, N. The Thermal Decomposition of Dimethyl Ether in the Presence of Hydrogen Sulfide ..... 328
IMAIZUMI, S. See MITSUI, S., 774.
IMAMURA, A. See FUKUI, K., 1076. 1224.
IMANISHI, S. See INUZUKA, K., 467.
IMOTO, M. Vinyl Polymerization. XLVII..... 26
XLVIII ..... 186
INAMOTO, N. 4, 5-Dimethoxycanthin-6-one and 2,6-Dimethoxy-*p*-benzoquinone from *Picrasma ailanthoides* Planchon ..... 888
INOKAWA, S. Studies on the Mucilage of the Root of "Tororo-aoi" (*Abelmoschus manihot*, MEDIC). III ..... 29
INOKUCHI, H. On the Electrical Conductivity of the Organic Thin Films: Perylene, Coronene and Violanthrene..... 749
INOKUCHI, H. The Photovoltaic Behavior in Organic Compounds .....1093
INOUE, E. See KOKADO, H., 705.
INOUE, M. See FUJINO, M., 740.
INOUE, M. Constituents of the Antibiotic, Glumamycin..... 885
INOUYE, H. Mass Spectrometric Study on Absorption of Water Vapor on a Graphite Surface ..... 643
INOUYE, K. Syntheses of Peptides Related to the *N*-Terminal Structure of Corticotropin. I..... 1
II ..... 4
INUZUKA, K. Calculation on the Electronic States of the Acrolein Molecule by the Semi-Empirical Molecular Orbital Method..... 6
INUZUKA, K. Effect of Solvent on Carbonyl Stretching Frequency of Ketones..... 467
INUZUKA, K. Electronic and Vibrational States of Acrolein ..... 729
INUZUKA, K. π-Electronic Structure of Cinnamaldehyde.....1557
ISEMURA, T. See IKEDA, S., 416. 422.
ISEMURA, T. Studies on Long Chain Alkyl Amides of Water-soluble Poly-α-amino Acids. I .....1236
ISHIDO, Y. New Catalysts for the Nucleoside Synthesis by Fusion Method.....1347
ISHIKAWA, T. An Analysis of Ishikawa's Equation of State as Applied to the CriticalRegion of Isopentane .....1329
ISHIMOTO, K. See MAEKAWA, K., 1221.
ISHIZAKI, M. See YAMADA, K., 1873.
ISOE, S. See NAKAZAKI, M., 741. 1189.
ITO, M. See INUZUKA, K., 467.
ITO, T. Cation-exchange Properties of Phosphoantimonic(V) Acid.....1736
ITŌ, Y. See UMEZAWA, S., 69. 1540.
IWAMOTO, T. Acid-Base Property and Metal Chelate Formation of 4-(2-Pyridylazo)-resorcinol ..... 605
IWAMURA, H. ŌKI, M., 1391. 1395.
IZUMI, Y. See AKAMATSU, A., 1067. 1302.
JANZ, G. J. Silanes. Vibrational Assignments and Frequency Correlations .....1495
KAJI, A. Studies on the Thiocarbamoylthiocarbonates. I ..... 254
II .....1147
KAKIHANA, H. See OHTAKI, H., 293.
KAKISAWA, H. See OKUMURA, Y., 895.
KAKIUTI, Y. Out-of-Plane Hydrogen Vibrations of *ortho*-, *meta*- and *para*-Deuterated Monosubstituted Benzenes..... 899
KAMADA, M. See TANAKA, N., 541.
KAMBE, H. Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. I.....1786
II .....1790
III .....1794
IV .....1797
KAMEMOTO, Y. See YAJIMA, S., 133. 493. 697.
KAMEOKA, H. Reaction of Hydrogen Peroxide on Fatty Acid Esters under Pressure. III... 626
KAMIKAWA, T. See TOKOROYAMA, T., 131.
KAMIYA, H. See ICHIKUNI, M., 1780.
KANAMORI, S. See SUGAWARA, K., 258.
KANAYA, M. See MORI, M., 1837.
KANEKO, T. On the Erlenmeyer Reaction. I...1314
KANOMATA, I. Mass-spectrometric Study on Ionization and Dissociation of Diethyl Ether by Electron Impact .....1596
KANOMATA, I. Mass-spectrometric Study on Ionization and Dissociation of Formaldehyde, Acetaldehyde, Aceton and Methyl Ethyl Ketone by Electron Impact .....1864
KATSUBE, Y. Spectrophotometric Determination of Beryllium, Copper and Iron with Sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate..... 72
KATSUBE, Y. Spectrophotometric Determination of Nitrite in Nitrate and Sulfate..... 743
KATSUBE, Y. Spectrophotometric Determination of Uranium with Sodium 2'', 6''-dichloro-4'-hydroxy-3,3'-dimethylfuchsone-5,5'-dicarboxylate ..... 826
KATO, H. Non-benzenoid Aromatic Heterocycles. IV ..... 357
V ..... 814
KATO, H. See FUKUI, K., 442, 851, 933, 1111.
KATO, H. See YONEZAWA, T., 707, 747.
KATO, M. See KURODA, Y., 877.
KATO, M. See OKUMURA, Y., 895.
KATO, S. Photoreduction of Acridine in Deaerated and Aerated Ethanol Solutions.....1026

KATO, S. Organoboron Compounds. I.....1107
KATO, T. Partition Equilibria of 2-Methyl 5-Ethyl Pyridine in the Systems of Benzene-Water and Chloroform-Water ..... 47
KATO, T. Oxidation of 2-Methyl 5-Ethyl Pyridine to Isocinchomeronic Acid ..... 636
KAWAI, T. Molecular Structure Investigation of Chlorotrifluoroethylene by Electron Diffraction .....1472
KAWAMOTO, K. Dehydrogenation of Secondary Alcohols with Reduced Copper. III ..... 161
IV ..... 795
V ..... 799
KAWANAMI, J. Bile Acids and Steroids. XX... 509
XXI..... 671
KAWASHIMA, T. Determination of Lanthanum, Samarium and Europium in Manganese Nodules by Neutron Activation..... 701
KAZAMA, S. See KUWATA, T., 1978.
KIDA, S. See ODANI, H., 571.
KIDA, S. Investigation on Mixed Complexes. VI ..... 962
KIGOSHI, K. Tritium and Carbon-14 in the Tree Rings .....1738
KIGOSHI, K. Variation of the Atmospheric Carbon-14 in Recent Years at Tokyo.....1739
KIJIMA, I. See YOSHINO, T., 459.
KIJI, J. See HIROTA, K., 1213.
KIKUCHI, K. Synthesis and Reactions of Cyano- and Carboxytropones .....1610
KIKUCHI, S. See HONDA, K., 529.
KIKUCHI, Y. See WADA, K., 337.
KIKUCHI, Y. Microwave Spectrum of Propargyl Halides. II ..... 348
KIMIZUKA, H. See MATUURA, R., 1512.
KIMURA, K. Inorganic Extraction Studies on the System between Bis(2-ethyl hexyl)-orthophosphoric Acid and Hydrochloric Acid. II... 63
KIMURA, K. Interaction Polarization of the Hydrogen Bonded Complexes. II ..... 304
KIMURA, M. Infrared Spectra of Cyclohexanoxime and Cyclohexanoxime-*d*.....108
KINOSHITA, M. Studies on Antibiotics and Related Substances. XII..... 308
KINUGASA, T. See NAKASHIMA, R., 1740.
KISHIMOTO, K. See OHTA, M., 1402.
KISO, Y. See SHINAGAWA, M., 137.
KITAHARA, K. See NOZOE, T., 312. 611.
KITAHARA, Y. Fulvalmixene. I ..... 589
KITAHARA, Y. Studies on the Mechanism of Rearrangement Reaction of 2-Phenyl-4-bromotropone to 2-Phenylbenzoic Acid.....1359
KITAJIMA, S. See KATO, S., 1107.
KITANO, H. See YONEZAWA, T., 707.
KITANO, H. See FUKUI, K., 851.
KITAZAWA, T. See TADOKORO, H., 1209.
KOBAYASHI, H. Polyterpenes. III .....1123
KOBAYASHI, M. Infrared Spectra of Some Deuterated Crystalline Polystyrenes. II ..... 560
III .....1045
KOBAYASHI, Y. See HIROTA, K., 1213.
KODAMA, M. Application of RADME to the Chelatometric Determination of Metals Employing the Alternating Current Polarographic Method ..... 714
KODERA, K. The Scattering of Beams of Alkali Atoms in Various Gases. II..... 566
KOIKE, H. See NAKANISHI, K., 533.
KOIZUMI, J. See MARUHA, J., 1541.
KOIZUMI, M. See KATO, S., 1026.
KOIZUMI, M. See USUI, Y., 1049. 1651.
KOIZUMI, M., See WATANABE, A., 1086.
KOJIMA, K. Polyaddition Reaction of Diphenylsilane to Diallyl Carboxylate..... 18
KOJIMA, M. See MATSUURA, N., 411.
KOJIMA, R. See NAGASE, S., 1468.
KOKADO, H. Photoconductivity of Zinc Oxide under Different Ambient Conditions ..... 705
KOMORITA, T. See YASUMORI, I., 588.
KONAKA, Y. See FUKUI, K., 712.
KORI, M. See YAJIMA, S., 697.
KŌSHIRO, T. The Effects of Various Spinning Processes on the Fine Structure of Viscose Rayon Staples (Distribution of Chain Length of Oxidizing-hydrolyzed Residue) ..... 476
KOYAMA, M. Chemical Studies on Radioactive Indicators. XXIV .....1766
KUBO, M. See NAKAMURA, D., 142.
KUBO, M. See KIMURA, M., 1081.
KUBOTA, D. See MATSUDA, R., 649.
KUBOTA, H. See SOBUE, H., 883.
KUBOTA, T. See TOKOROYAMA, T., 131.
KUBOTA, T. Transformation of Swertiamarin to Gentiopicrin. The Structure of Gentiopicrin .....1345
KUBOTA, T. Chemical Constitution of Enmein a Bitter Principle from Isodon trichocarpus Kudo .....1737
KUDO, K. See GOTO, R., 753.
KUGE, T. Physicochemical Properties of Dilute Aqueous Solution of Amylose. Optical Rotatory, Viscometric and Osmometric Studies ...1264
KUMANOTANI, J. See KUWATA, T., 1978.
KUMASAKI, S. See NAKANISHI, K., 533.
KURAISHI, M. Fischer-Tropsch Synthesis with Tubular Reactor of 18.1 l. Catalyst Bed. I ..... 780
KURAISHI, M. Fisher-Tropsch Synthesis with Tubular Reactor of 18.1 l. Catalyst Bed. II .....1101
KURATA, M. See ODANI, H., 571.
KURATA, M. See TAMURA, M., 684.
KURITA, M. See KURAISHI, M., 780. 1101.
KURODA, H. See INOKUCHI, H., 749.
KURODA, Y. Infrared Spectra and the Structure of Some Metal-oxamide Complexes..... 877
KURODA, Y. See KIMURA, M., 1081.
KUROSAWA, E. Quinones. I ..... 300
KUWANA, M. See MISUMI, S., 1833.
KUWATA, K. Electron Spin Resonance and Electronic Absorption Spectra of the Radical Anions of Pyridine and Acridine..... 291
KUWATA, K. Electron Spin Resonance Study on Photolysis of Acetone and Benzophenone..... 458
KUWATA, T. Studies on Phenolic Resins. IV...1978
KYUNO, E. See MORI, M., 1837.
LAKSHMINARAYANAIAH, N. See SUBRAHMANYAN, V., 587.
MACHIDA, K. See UNO, T., 545, 551, 821, 1448.
MACHIDA, S. Chemical Studies on Wood Hemicelluloses. III..... 916

MAEDA, K. On the pd Hybridization of the Sulfur Atom in Thiothiophten. I ..... 785
II .....1166
MAEKAWA, K. Reaction of Trypsin with *S*-Methylisothiourea and with *S*-Methylglucosylisothiourea .....1221
MAKI, N. Polarographic Studies of Metallic Complexes. VI ..... 891
MALIK, W. U. Studies on the Composition and Properties of Less Familiar Metal Cyano Complexes. I .....1306
II .....1310
MARUHA, J. Effect of Impurities on the $^{81}Br$ Quadrupole Resonance in *p*-Dibromobenzene...1541
MARUYAMA, A. On the Temperature Dependence of Spectra of Solvated Anions .....1243
MARUYAMA, K. Oxidizing Action of Hydroperoxides. V ..... 102
VI ..... 105
MARUYAMA, Y. See INOKUCHI, H., 1093.
MASAKI, M. Über die Einwirkung von Brom auf 9-Acetylfluoren.....1257
MASE, H. On the Reactivity of Various Silicate Minerals toward Acids..... 214
MASUBUCHI, Y. See TADA, R., 209.
MASUDA, S. See INAMOTO, N., 888.
MASUMURA, M. See HORIE, T., 1547.
MATHUR, P. B. A Diffusion Mechanism for Liesegang Rings. I ..... 437
MATHUR, P. B. Structural Analysis of Liesegang Ring Systems ..... 440
MATSUBARA, A. See MATUURA, R., 1512.
MATSUBARA, I. Spectroscopic Studies on Molecular Configurations of Some Aliphatic Dinitriles. I .....1710
II .....1719
MATSUBARA, S. Synthesis of $\alpha$-Maltosides. I ... 718
MATSUDA, M. Decomposition of Mono- and Diethanolamine Carbamate in Glycerol Solution .....1665
MATSUDA, R. Kolbe's Reaction of Higher Fatty Acids. II ..... 649
MATSUI, K. See NOZOE, T., 616, 1382.
MATSUKI, Y. See TAKAHASHI, K., 1599.
MATSUMOTO, T. A Synthesis of an Octahydrophenanthrene Derivative ..... 274
MATSUMOTO, T. See SUZUKI, A., 455.
MATSUMURA, C. See WADA, K., 337.
MATSUMURA, S. The Structure of the Condensation Products of Troponoids and Ethyl Cyanoacetate ..... 995
MATSUMURA, S. Condensation Reaction of Troponoids and Ethyl $\alpha$-Cyano-$\beta$-aminoglutaconate. I .....1361
MATSUNAGA, Y. See HARADA, Y., 585.
MATSUNAGA, Y. Electron Spin Resonance of Tetracene-Antimony Pentachloride ..... 893
MATSUNAGA, Y. Note on the Electron Spin Resonance of Cupric Oxide-Alumina Catalysts .....1291
MATSUNAGA, Y. Note on the Oxidation of Perylene in Strong Acids.....1293
MATSUNAGA, Y. Refractometric Study of Some Cyano and Oxalato Complex Anions.....1563
MATSUNO, S. See ANDO, J., 678.
MATSUOKA, S. See YONEZAWA, T., 707.
MATSUURA, N. Studies on Extraction of Polonium(IV) by Hexone from Acid Solution..... 411
MATSUURA, T. See KUBOTA, T., 1737.
MATUURA, R. The Effect of Alcohols on the Solubilization of Oleic Acid in the Aqueous Solution of Sodium Dodecyl Sulfate ..... 395
MATUURA, R. See SHIMOZAWA, R., 457.
MATUURA, R. The Study of Adosorption of Detergents at a Solution-Air Interface by Radiotracer Method. IV.....1512
MESHI, T. See SATO, Y., 167. 243.
MIDORIKAWA, H. See IGARASHI, M., 1543.
MIIDA, S. See MATUURA, R., 395.
MIKAWA, Y. See JANZ, G. J., 1495.
MINAGAWA, S. See KATO, S., 1026.
MISUMI, S. Alternant Conjugate Systems. I ...1827
II .....1833
MITA, I. See KAMBE, H., 1797.
MITSUI, S. Stereochemistry and Mechanisms of Catalytic Hydrogenolysis and Hydrogenation. I ..... 774
MITSUTOMI, A. Forschung über den katalytischen Abbau des Kolophoniums .....1319
MITSUTOMI, A. Forschung über den Katalytischen Abbau des rohen Kieferharzes .....1325
MITSUTOMI, A. Forschung über die katalytische Entwässerung des Isoamylalkohols. I .....1518
II .....1525
III .....1693
IV .....1698
MIYAKE, A. See FUJINO, M., 740.
MIYAKE, C. Magnetic and Spectrophotometric Studies on the Decoloration of Thiocyanatoiron(III) Complexes in Solutions. II..... 471
III ..... 475
MIYAKE, Y. See TAKAHASHI, K., 1599.
MIYAMOTO, M. Absorptiometric Determination of Micro-amounts of Iron in Nuclear Grade Graphite and Urania-Graphite Fuel; Nitroso R Salt Method after Coprecipitation of Iron with Manganese Dioxide.....1435
MIYAZAWA, T. Infrared Studies of the Librations of Water Molecules in the Solid Matrices at 20°K ..... 202
MIYAZAWA, T. Internal Rotation and Low Frequency Spectra of Esters, Monosubstituted Amides and Polyglycine ..... 691
MIZUNO, K. Structure of Enteromycin. I .....1419
II .....1425
III .....1631
IV .....1633
MOCHIZUKI, Y. See KAWASHIMA, T., 701.
MOOKHERJI, A. Diamagnetic Behavior of Some Aliphatic Molecules in Crystals ..... 233
MOOKHERJI, S. N. See MOOKHERJI, A., 233.
MORI, M. The Crystal Structure of $[Cr(NH_3)_6][CuCl_5]$ ..... 295
MORI, M. On Some Dark-colored Chlorocuprates (I, II) and Related Compounds. II ..... 454
III .....1249
MORI, M. Thermodynamic Studies on Cobalt Complexes. VIII.....1757
IX .....1761
MORI, M. Adsorbabilities of Diacidotetrammine Type Cobalt(III) Complex Ions on a Cation-exchanger .....1809

MORI, M. Preparation and Absorption Spectra of the Cobalt(III) Complexes of Amino Acide ....1837
MORI, N. Rates of Solvolysis of Di-*p*-toluenesulfoxycyclohexanes .... 110
MORI, N. Conformation and Reactivity of 4-Methylcyclohexylmethyl *p*-Tosylates ....1299
MORI, N. The Preparation of *cis*- and *trans*-4-*tert*-Butylcyclohexyl-1-carbinols....1567
MORI, Y. Electronic Structure of Benzyl Radical ....1031
MORI, Y. The Effect of Electron Transfer in the Electronic Structure of Benzyl Radical ....1035
MORI, Y. Mercury Photosensitized Decomposition of Carbon Dioxide by 1849 Å ($Hg\ 6^1p_1$) ....1128
MORINAGA, K. The Chemical Reaction in Silent Electric Discharge. I .... 157
MORINO, Y. See WADA, K. 337.
MORINO, Y. See HIROTA, E., 341.
MORINO, Y. See KIKUCHI, Y., 348.
MORITANI, I. The Effect of Conformation on Reactivity. III ....1334
MOROKUMA, K. See FUKUI, K., 230, 1178, 1224.
MOROKUMA, K. See YONEZAWA, T., 747.
MUKAI, T. See NOZOE, T., 619. 1384.
MUKAIYAMA, T. The Dehydration Reactions by Means of Esters of Phosphoric Acid .... 99
MUKAIYAMA, T. The Preparation of Diethyl Phosphate .... 812
MURAGISHI, K. See NAKAGAKI, M., 316.
MURAHASHI, S. See TADOKORO, H., 381. 1209.
MURAHASHI, S. Polymerization of Allyl Chloride by Ziegler's Catalyst.... 631
MURAHASHI, S. Stereoregular Polymers. VIII .... 939
MURAHASHI, S. See NOZAKURA, S., 1673.
MURAKAMI, M. See MORITANI, I., 1334.
MURASHIMA, K. See MISUMI, S., 1833.
MURATA, I. The Structure of 4-(α-Ethylenedioxy)-ethyltropolone Methyl Ether .... 577
MURATA, I. 5- and 2, 5-Substituted 1, 3-Diazaazulenes .... 580
MURATA, I. See KITAHARA, Y., 589. 1359.
MURATA, M. See TAMURA, M., 684.
MUROI, T. See KITAHARA, Y., 1359.
MUROI, T. The Acid Product obtained in the Synthesis of 2-Phenyltropone Derivatives from 2-Phenylsuberone .... 178
NAGAHAMA, S. See KOBAYASHI, H., 1123.
NAGAI, H. See TADOKORO, H., 1504.
NAGAI, K. Studies on Isoprenoid. XIII ....1825
NAGASE, S. Preparation of Perfluorocarboxylic Acids from Esters by Electrochemical Fluorination ....1468
NAGASE, T. Einwirkung von Thionylchlorid auf Diarylathinylcarbinolen .... 139
NAGATA, C. See FUKUI, K., 37. 230. 712. 933. 1076. 1224.
NAGATA, I. See TAMURA, M., 684.
NAGOSHI, K. See HIROTA, K., 226.
NAKADA, F. Dehydration of Bile Acid and their Derivatives, VIII .... 538
NAKAGAKI, M. Colloid Chemical Studies on Starching Materials. III.... 316
NAKAGAKI, M. Optical Properties of Colored Colloidal Systems. II .... 433
NAKAGAKI, M. Theory on the Light Scattering of High Polymer Solutions Considering the Anisotropy of Segments .... 834
NAKAGAWA, K. See OKAZAKI, N., 983.
NAKAGAWA, M. See TODA, F., 862. 874. 1000.
NAKAGAWA, M. See MISUMI, S., 1833.
NAKAGAWA, N. Solvent Shift of Methyl Proton Nuclear Magnetic Resonance.... 143
NAKAJIMA, K. A New Method for the Preparation of Piperazines. I .... 651
II .... 655
III ....1218
NAKAMURA, A. New Stable Olefin Complexes of Cobalt(I).... 452
NAKAMURA, D. Nuclear Quadrupole Resonance of *B*-Trichloroborazole.... 142
NAKAMURA, E. Distribution of Neptunium between Di-(2-ethyl hexyl)-phosphoric Acid and Mineral Acids.... 402
NAKAMURA, H. Study on Metal Complexes of Analytical Importance. I ....1143
NAKANISHI, K. Ultraviolet Spectra of *N*-Heterocyclic Systems. I .... 53
II .... 533
NAKANISHI, K. See TAMURA, M., 684.
NAKASHIMA, R. Dipole Moment and Infrared Spectrum of 2, 3, 5, 6-Tetraisopropylnitrobenzene....1740
NAKAZAKI, M. Alkylation of Sodio-2,3-dimethylindole and Sodio-tetrahydrocarbazole in Nonpolar Solvent .... 334
NAKAZAKI, M. The Absolute Configuration of Rotenone .... 453
NAKAZAKI, M. The Structure of Todomatuic Acid. Synthesis of (±)-Dihydro-desoxotodomatuic Acid.... 741
NAKAZAKI, M. A Novel Synthetic Route of 3,6-Dimethyl-2, 3-dihydro-1*H*-cyclopent[*a*]anthracene and 6-Methyl-2, 3-dihydro-1*H*-cyclopent-[*a*]anthracene ....1189
NAKAZAKI, M. The Absolute Configuration of Rotenone ....1246
NAMBA, Y. The Crystal Structure of Phenazine-5,10-dioxides .... 889
NAYA, K. See KUBOTA, T., 1737.
NEGORO, K. Studies on Micro-paraffin. III....1366
IV ....1374
NEOGY, D. See MOOKHERJI, A., 233.
NEZU, H. See SHINAGAWA, M., 445.
NISHIDA, H. See WATANABE, T., 1285.
NISHIDA, S. See MORITANI, I., 1334.
NISHIKORI, S. See MACHIDA, S., 916.
NISHIMURA, N. Abnormal Acceleration of the Rate of Bulk Polymerization of Styrene ....1158
NISHIMURA, S. Hydrogenation and Hydrogenolysis. V .... 32
NISHIMURA, S. Rhodium-Platinum Oxide as a Catalyst for the Hydrogenation of Organic Compounds. II ....1544
NISHIYAMA, Y. See TADOKORO, H., 381.
NISHIZAWA, Y. Studies on Organophosphorus Compounds. I .... 688
II ....1170
III ....1205
NITTA, I. See TOMITA, K., 286.

NITTA, I. The Crystal Structure of Orthorhombic Aniline Hydrobromide, $C_6H_5NH_3Br$.....1405
NITTA, I. See TADOKORO, H., 1504.
NIWA, K. See MARUYAMA, A., 1243.
NOGUCHI, J. See ISEMURA, T., 1236.
NOMURA, Y. Syntheses and Ultraviolet Spectra of Aromatic Azo Compounds. I .....1648
NORTON, C. J. Naphthalene as an Isolatable Reaction Intermediate in the Catalytic Vapor-phase Oxidation of Methylnaphthalenes to Phthalic Anhydride .....1545
NOZAKI, T. Chemical Use of the Absorption of Soft $\gamma$-Rays, $\beta$-Ray-excited X-Rays and K-Capture S-Rays. I .....1769
NOZAKURA, S. See TADOKORO, H., 381. 1209.
NOZAKURA, S. See MURAHASHI, S., 631. 939.
NOZAKURA, S. Stereoregular Polymers. IX.....1673
NOZOE, T. Syntheses of Benzo[b]tropothiazine and its Derivatives..... 146
NOZOE, T. On Oxazolo[5 : 4-b]tropones..... 312
NOZOE, T. A Ring-Chain Tautomerism in the Reaction Products of 3-Aminotropolone and Some Ethoxymethyleneacetates ..... 611
NOZOE, T. A Note on the Ring-Chain Tautomerism in the Reaction Products of *o*-Aminophenol and Some Ethoxymethyleneacetates ... 614
NOZOE, T. On the Structure of 2-Mercaptotropones ..... 616
NOZOE, T. Reaction of Troponoids and Organometallic Compounds. VI ..... 619
NOZOE, T. Diels-Alder Reaction of Troponoids. II ..... 623
NOZOE, T. On 2-Amionotropothione Derivatives. .....1382
NOZOE, T. Synthesis of Some 8,8-Disubstituted Heptafulvene Derivatives.....1384
NUKADA, K. Infrared and Raman Spectra of Dialkoxy Methanes in Various Phases and the Assignment of Spectra of Methoxy Ethoxy Methane .....1615
NUKADA, K. Infrared and Raman Spectra of Diethoxy Methane and Diethoxy Methane-$d_2$ .....1624
OAE, S. Mechanisms of the Wallach Rearrangement .....1873
OBATA, H. See USUI, Y., 1049.
OBATA, H. Phototreduction of Methylene Blue by Visible Light in the Aqueous Solution Containing Certain Kinds of Inorganic Salts. II .....1057
OCHI, M. See YOSHINO, T., 459.
ODA, D. Reactions of Quinaldil and its Related Compounds with Alkali. I ..... 557
ODA, T. See NAMBA, Y., 889.
ODANI, H. Diffusion in Glassy Polymers. I ... 571
II ..... 817
OGATA, N. The Resonance Effect of Amide Group on the Polymerizability of Lactam Derivatives. I..... 245
II ..... 248
OGATA, N. Studies on Polymerization and Depolymerization of $\varepsilon$-Caprolactam Polymer. IX .....1201
OGATA, Y. The Relation between Reactivity and Selectivity ..... 604
OGAWA, K. See KURAISHI, M., 780. 1101.
OGAWA, T. See KUWATA, K., 291.
OGIHARA, T. See SHIOTA, M., 40.
OGINO, H. See TANAKA, N., 1040.
OGINO, K. The Mechanical Behavior of Swollen Polystyrene. Poly-*p*-chlorostyrene and their Copolymers in Benzene. II ..... 153
OGURA, J. See KAKIUTI, Y., 899.
OGURA, K. The Mannich Base of Troponoid and its Application. V..... 839
OHASHI, M. See NAKANISHI, K., 533.
OHASHI, S. Determination of Ortho-, Pyro- and Tripolyphosphate by the Use of a Small Column of Ion-exchange Resin.....1516
OHGO, Y. See YOSHIMURA, J., 1197.
OHNO, S. See HOTTA, H., 1640.
OHTA, H. See YAMADA, H., 241.
OHTA, M. See HASHIMOTO, M., 668.
OHTA, M. Studies on Meso-ionic Compounds. XIV.....1402
OHTA, M. See KATO, H., 357. 814.
OHTA, M. See MASAKI, M., 1257.
OHTAKI, H. A Method for Estimation of the Hydration Numbers of Ions in Ion Exchange Resins..... 293
OHYAMA, T. The Effects of pH on the Flocculation of Quartz Aqueous Suspensions ..... 790
OKA, S. Studies on Lactone Formation in Vapor Phase. I ..... 12
OKABAYASHI, H. Kerr Effect in Liquid State ...1010
OKAMOTO, K. Polarographic Studies of Some Organo-sulfur Compounds. I ..... 920
OKAMOTO, K. A. C. Polarography of Thiamine Hydrochloride in Weakly Acidic Buffer Solutions .....1063
OKAMOTO, K. Kinetic Studies on Solvolysis. VI .....1131
VII .....1137
OKAZAKI, N. A Study of Dehydration and Hydration of Oxalic Acid by Means of the Deuterium Exchange Reaction ..... 977
OKAZAKI, N. Deuterium and Oxygen-18 Tracer Study of the Dehydration and the Hydration of Copper Sulfate ..... 983
OKAZAKI, N. A Study of Dehydration and Hydration of Sodium Dihydrogen Phosphate and Racemic Acid by Means of the Deuterium Exchange Reaction..... 985
OKAZAKI, N. The Rearrangement of *N*-Deuterated Aromatic Amine Hydrochloride into its Ring-deuterated Analogue in the Solid Phase : The Rearrangements of *o*- and *m*-Toluidine Hydrochlorides and the Effect of Anions on the Rate of Rearrangement of Anilinium Salts ..... 989
ŌKI, M. Intramolecular Hydrogen Bonding in $\alpha$-Keto and $\alpha$-Alkoxycarboxylic Acids. III... 374
IV ..... 378
ŌKI, M. Intramolecular Interaction between Hydroxyl Group and $\pi$-Electrons. XIII .....1391
XIV.....1395
OKUDA, T. The Polymerization of $\gamma$-Methyl-L-glutamate *N*-carboxyanhydride Initiated with Acetic Acid .....1872
OKUMURA, A. See OKAZAKI, N., 983. 985. 989.
OKUMURA, F. S. See HORIE, T., 1547.
OKUMURA, Y. The Structure of Tanshinone-II ..... 895

OMURA, I. Mass Spectra at Low Ionizing Voltage and Bond Dissociation Energies of Molecular Ions from Hydrocarbons....1227
ONO, S. See WASA, T., 518.
ONO, S. See KUGE, T., 1264.
OSAKA, K. See NOZOE, T., 1384.
OSAWA, M. See KAWASHIMA, T., 701.
OSAWA, R. See NAKADA, F., 538.
OSHIMA, H. $n$-$\pi$Absorption Spectra of Some Aliphatic Aldehydes .... 846
OTANI, S. See GOTO, R., 753.
OTSUKA, H. See INOUYE, K., 1. 4.
OUCHI, A. See MATSUURA, N., 411.
OUCHI, A. See YOSHINO, Y., 1194.
OYOSHI, A. See SHINAGAWA, M., 137.
RYANG, M. On the Formation of Benzoin by the Reaction of Carbon Monoxide with Organometallic Compounds ....1341
SAËKI, S. The Infrared Absorption Spectrum of 1,2,4,5-Tetrachlorobenzene in Vapor State ...1552
SAËKI, S. Raman Spectra of $p$-Dichlorobenzene and $p$-Dichlorobenzene-$d_4$ ....1658
SAËKI, S. The Raman Spectra of 1,3,5-Trichlorobenzene and 1,3,5-Trichlorobenzene-$d_3$....1851
SAËKI, S. Raman Spectra of 1,2,4,5-Tetrachlorobenzene and 1,2,4,5-Tetrachlorobenzene-$d_2$ ...1858
SAISHO, H. Solvent Extraction of Inorganic Nitrates with Diphosphonate Ester. I .... 859
II ....1254
SAITO, T. Proton Magnetic Resonance Studies on the Thermally Dehydrated Products of Alumina Trihydrate .... 757
SAITO, T. Some Observations on the Process of Dehydration and Rehydration of Gypsum by Means of Proton Magnetic Resonance ....1454
SAITO, Y. See MORI, M., 295.
SAITO, Y. See SOBUE, H., 1343.
SAKAKIBARA, S. Studies on Dehydroalanine Derivatives. III .... 205
IV .... 171
V .... 174
SAKAKIBARA, S. See AKABORI, S., 739.
SAKUDA, Y. Oxidation of *l*-Dihydrocarveol and its Acetate with Selenium Dioxide .... 514
SAKUMOTO, A. Radiation-induced Reaction in an Aqueous Benzoic Acid Solution. I .... 660
II .... 663
SAKURAI, S. See OKUDA, T., 1872
SANO, M. Semiconductivity and Absorption Spectrum of Perylene Single Crystal ....1569
SANO, M. Photoconductivity of Polycyclic Aromatic Compounds ....1668
SATA, T. Phase Relationship in System 3CaO-$P_2O_5$-Mgo-$SiO_2$.... 113
SATAKE, K. See WATANABE, T., 1285.
SATAKE, K. Reactions of Picryl Ether with Amino Compounds ....1346
SATO, T. See YOSHIMURA, J., 1197.
SATO, T. See ISHIDO, Y., 1347.
SATÔ, G. See TANAKA, N., 541.
SATOH, T. The Viscosity of Concentrated Aqueous Solutions of Strong Electrolytes ....1260
SATO, Y. Studies on Tritium Labeled Compounds. II .... 167
IV .... 169
SATO, Y. Studies on Heavy-Nitrogen Labeled Compounds. III .... 243
SEKI, S. See TADOKORO, H., 1504.
SEKINE, H. See KAWAI, T., 1472.
SEMBA, K. Absorption Spectra of Nitrobenzene Derivatives. II .... 722
SENŌ, M. See YAMABE, T., 738.
SENŌ, M. Aggregation of Ion-exchange Resin Particles....1002
SENŌ, M. Ion-exchange Behavior of Acidic and Basic Amino Acids ....1021
SENŌ, M. On the pH Dependence of Transport Behavior of Weak Acids and Weak Bases across Ion-exchange Membranes ....1741
SHANMUGASUNDARAM, V. See SRIRAMAN, S., 1288.
SHIBA, K. See YAJIMA, S., 133. 493. 697.
SHIBA, S. Visco-elastic Behaviors of Aluminum Soap-Hydrocarbon Systems. I .... 194
II .... 198
SHIBA, S. Differential Thermal Analysis of Aluminum Soaps .... 804
SHIBA, S. Differential Thermal Analysis of the Systems Aluminum Soap-Hydrocarbon .... 809
SHIBATA, M. See MORI, M., 1809. 1837.
SHIBATA, N. See BABA, H., 590.
SHIBATA, R. See HAYASHI, T., 1116.
SHIMA, S. See SATAKE, K., 1346.
SHIMADA, A. The Crystal Structure of $p$-Aminobenzenearsonic Acid .... 639
SHIMANOUCHI, T. Normal Coordinate Treatment and Assignment of Infrared Absorption Bands of Polyvinyl Chloride .... 359
SHIMOIIZAKA, J. See OHYAMA, T., 790.
SHIMOJI, M. See MARUYAMA, A., 1243.
SHIMONISHI, Y. See AKABORI, S., 739.
SHIMOZAWA, R. The Interaction of a Surfactant with a Monolayer Studied by Radiotracer Method .... 457
SHIMURA, Y. See NAKAMURA, H., 1143.
SHINAGAWA, M. Rapid Separation of Nuclides in Fission Products and their Determinations by Focussing Chromatographic Method.... 137
SHINAGAWA, M. Studies on the Catalytic Double Wave of Cystine by Oscillographic Polarography .... 445
SHINGU, H. See OKAMOTO, K. 1131. 1137.
SHINODA, K. The Surface Tension and the Critical Micelle Concentration in Aqueous Solution of $\beta$-D-Alkyl Glucosides and their Mixtures .... 237
SHIOTA, M. The Formation and the Reactions of 3$\alpha$-Chloro-5,6$\beta$-epoxy-5$\beta$-cholestane .... 40
SHISHIDO, N. See NOZOE, T., 1384.
SIMAMURA, O. See INAMOTO, N., 888.
SOBUE, H. The Crystallinity of Polyaldehydes .... 883
SOBUE, H. Effects of High Energy Ionizing Radiation on Crystallinities of Cellulose II, III and IV....1343
SODA, R. On the Structures of *p-tert*-Butyl Phenol Resin and $\alpha$-Naphthol Resin. II....1482
III ....1491
SOEMATSU, I. See IMOTO, M., 26.
SONE, K. See KURODA, Y. 877.

SONODA, N. Hydrogen Peroxide Oxidation. V ....1006
SRIRAMAN, S. Thermo-magnetic Study of Mercury and Dilute Amalgams of Sodium and Potassium ....1288
SRIRAMAN, S. The Diamagnetic Susceptibility of Benzoate, Salicylate, Propionate, Butyrate and Succinate Ions ....1560
SRIVASTAVA, J. P. See DESHMUKH, G. S., 325.
SUBRAHMANYAN, V. Electro-osmotic Permeability of Cation Exchange Membranes .... 587
SUGA, H. On the Orientational Order-Disorder Transition in Crystalline Aniline Hydrobromide .... 426
SUGAWARA, K. Spectrophotometric Determination of Submicrogram Quantities of Orthophosphate in Natural Waters.... 258
SUGIMORI, A. The Competitive Reduction of Nitrobenzene and Para-Substituted Nitrobenzenes with Nickel Catalysts .... 407
SUGIMORI, A. Radiolysis of Crystalline Oxalate Complexes .... 449
SUGIMOTO, N. See SATO, Y., 243.
SUGIURA, T. Energy Distiribution of Secondary Electrons from Copper-Beryllium Alloy by Positive Ions of Inert Gases. I ....1475
SUHARA, M. See MARUHA, J., 1541.
SUGIURA, T. Secondary Electron Emission from Copper-Beryllium (4%) Surface by Bombardment of Various Positive Ions .... 58
SUZUKI, A. See MATSUMOTO, T., 274.
SUZUKI, A. The Nuclear Magnetic Resonance Spectra of Some Aconite Bases : *Lucaconine and Luciduscline* .... 455
SUZUKI, K. See IKEDA, N., 1705.
SUZUKI, M. See MORINAGA, K., 157.
SUZUKI, N. See NAKANISHI, K., 53.
SUZUKI, R. See HIGUCHI, I., 1539.
SUZUKI, S. See BABA, H., 82.
SUZUKI, S. See YASUMORI, I., 588.
SUZUMURA, H. Isolation of 2,3-Cyclopenteno-5-methylpyridine from Coal Tar Bases....1097
SUZUMURA, H. Synthesis of Phenanthryl Phenyl Ethers....1822
SUZUMURA, H. Separations of Lutidines Collidines and 2,3-Cyclopentenopyridines from Coal Tar Bases ....1846
TABUSHI, I. See OGATA, Y., 604.
TACHIKAWA, E. Neutron and $\gamma$-Irradiation of Propionamide .... 770
TACHIKAWA, T. On the Reaction of Aromatic Dinitriles and Formaldehyde.... 48
TACHIKAWA, T. On the Oxidation of $\beta$-Aminopropionitrile. II .... 461
III .... 464
TADA, R. The Beckmann Rearrangement of the Geometrical Isomers of Cyclohexyl Phenyl Ketoxime in Liquid Sulfur Dioxide .... 209
TADA, R. See TOKURA, N., 270. 1812.
TADOKORO, H. Stereoregular Polymers. VII ... 381
TADOKORO, H. Infrared Spectra of Isotactic Poly-$\alpha$-olefins ....1209
TADOKORO, H. Syntheses and Infrared Absorption Spectra of Deuterated Polyvinyl Alcohols $-(-CD_2-CD-)_n-$ ....1504
OH(D)
TAGUCHI, I. An X-Ray Study on the Phase Transition of Aniline Hydrobromide, $C_6H_5NH_3Br$ .... 392
TAGUCHI, I. See NITTA, I., 1405.
TAIRA, S. Reduction of Organic Compounds with Urushibara Catalysts under High Pressure. VII .... 261
TAIRA, S. Reduction of Organic Compounds with Urushibara Catalysts under High Pressure. VIII ....1072
IX ....1294
TAKAGI, M. See WASA, T., 518.
TAKAGI, M. Polarographic and Spectrophotometric Studies on Trimethylpyruvic Acid..... 905
TAKADA, T. See OHASHI, S., 1516.
TAKAHASHI, K. See NOZOE, T., 146.
TAKAHASHI, K. See KOKADO, H., 705.
TAKAHASHI, K. Proton Magnetic Resonance Spectra of Methylthiophenesulfonylchlorides ....1599
TAKAHASHI, T. See SATO, Y., 167. 169.
TAKAI, N. See YAMABE, T., 738.
TAKEKIYO, S. Non-empirical Study of the $\pi$-Electronic Structure of Vinyl Chloride Molecule by Valence Bond Method ....1466
TAKEKIYO, S. Non-Empirical Calculation of the $\pi$-Electronic Structure of Cyclobutadiene Molecule by Valence Bond Method....1686
TAKEMOTO, K. See IMOTO, K., 186.
TAKEMURA, E. See OKAZAKI, N., 977.
TAKEMURA, F. See HIROTA, K., 1340.
TAKEUCHI, K. See OKAMOTO, K. 1137.
TAKEUCHI, S. See NOZAKURA, S., 1673.
TAMURA, M. See ODANI, H., 571. 817.
TAMURA, M. An Empirical Method for Estimating Normal Boiling Point and other Physical Properties of Alkene Hydrocarbons .... 684
TAMURA, M. See HAGIHARA, N., 892.
TAMURA, T. See KODERA, K., 566.
TANAKA, K. See BABA, H., 590.
TANAKA, M. See SATAKE, K., 1346.
TANAKA, N. The Composition and the Solubility Product Constant of Lead(II) Ethylenediaminetetraacetatoplumbate(II) .... 541
TANAKA, N. Polarographic Determination of the Formation Constant of Sulfatonickel(II) Complex ....1040
TANAKA, T. The Synthesis of 3-$\alpha$-Carboxyethylcyclopentanol Lactone .... 888
TANAKA, T. Normal Vibrations of Dimethyldimethoxysilane ....1752
TANIMOTO, F. See FUKUI, K., 851.
TARAMA, K. The Electron Spin Resonance Absorption of Vanadium Pentoxide Catalysts ...1195
TASUMI, M. See SHIMANOUCHI, T., 359.
TERANISHI, S. See TARAMA, K., 1195.
TEZUKA, T. See NOZOE, T., 619.
THIRUVENGADATHAN, S. See SRIRAMAN, S., 1560.
TOBISAWA, S. Thermal Decomposition of Potassium Chlorate.... 89
TODA, F. Cyclic Acetylenes. V .... 862
VI .... 874
TODA, F. Oxidation of *o*-Hydroxyphenylacetylene and *o*, *o'*-Dihydroxydiphenyldiacetylene by Copper Ion ....1000
TOKIWA, F. See ISEMURA, T., 1236.

TOKOROYAMA, T. Natural Furan Derivatives. V ..... 131
TOKURA, N. See TADA, R., 209.
TOKURA, N. Formation of Cyclohexano[*c*]1,2,5-oxadiazole from 1,2-Cyclohexanedione Dioxime. An Attempted Beckmann Rearrangement with Thionyl Chloride in Liquid Sulfur Dioxide ..... 270
TOKURA, N. The Beckmann Rearrangement of 1,2-Cyclohexane-dione Dioxime in Liquid Sulfur Dioxide .....1812
TOMIKURA, Y. See KIGOSHI, K., 1738.
TOMITA, K. Über die Kupfer-salze der ω-Aminosäure. I ..... 280
II ..... 286
III ..... 297
TOMITA, Y. See KUBOTA, T. 1345.
TONOMURA, T. See MARUHA, J., 1541.
TOYAMA, O. See IMAI, N., 328.
TOYODA, S. Analysis of Variation of Coil Character by Aqueous Solution with Q-Meter..... 944
TOYOOKA, Y. See NOZOE, T., 623.
TOYOSHIMA, Y. A New Rapid Method of Determining Molecular Weight of Water Soluble Linear Polymers by the Measurement of Rate of Settling of Clay Suspensions .....1734
TSUCHIDA, R. See MAKI, N., 891.
TSUCHIDA, R. See NAKAMURA, H., 1143.
TSUCHIHASHI, G. See SUGIMORI, A., 449.
TSUCHIHASHI, G. See SAKUMOTO, A., 660. 663.
TSUCHIHASHI, G. See TACHIKAWA, E., 770.
TSUCHIYA, S. Studies on the Chemical Equilibrium Lag during the Rapid Expansion through the Rocket Nozzle..... 854
TSUDA, Y. Infrared Spectra of Polyacrylonitrile Polymerized by Gamma-irradiation at Low Temperatures .....1046
TSUMAKI, T. See YAMADA, H., 241.
TSUNODA, Y. See KATO, T., 47.
TSUNODA, Y. See YOSHINO, Y., 1194.
TSURUIZUMI, A. Studies on the Surface Structure of Porous Materials .....1457
TSUTSUI, T. See KUBOTA, T., 1737.
TSUTSUMI, H. See MATUURA, R., 395.
TSUTSUMI, S. See SONODA, N., 1006.
TSUTSUMI, S. See RYANG, M., 1341.
TSUYUKI, T. See INAMOTO, N., 888.
TSUZUKI, Y. See KATO, S., 1107.
TSUZUKIDA, Y. See SATAKE, K., 1346.
UCHIDA, H. See KURAISHI, M., 780. 1101.
UCHIKAWA, H. See YAMAGUCHI, G., 1536.
UCHIDA, T. Organic Semiconductors with High Conductivity. III .....1015
UESUGI, K. See KATSUBE, Y., 72. 743. 826.
UEYANAGI, J. See FUJINO, M., 740.
UMEZAWA, S. Studies on Antibiotics and Related Substances. XI ..... 69
UMEZAWA, S. See KINOSHITA, M., 308.
UMEZAWA, S. See ZEN, S., 890.
UMEZAWA, S. Synthesis of 4,6-Di-(D-glucopyranosyl)deoxystreptamine .....1540
UNO, T. Infrared Spectra of Acyclic Imides. I ..... 545
II ..... 551
III ..... 821
IV .....1448
URUNO, S. See ICHIKAWA, F., 952.
USHIKI, Y. See HIGUCHI, I., 1539.
USUI, S. See OHYAMA, T., 790.
USUI, Y. Photoreduction of Methylene Blue by Visible Light in the Aqueous Solution Containing Certain Kinds of Inorganic Salts. I .....1049
II .....1057
III .....1651
WADA, K. Microwave Spectrum and Molecular Structure of Monochloroacetonitrile, $CH_2ClCN$ ..... 337
WADA, G. A Simplified Model for the Structure of Water ..... 955
WAINAI, T. See FUJIWARA, S., 881.
WAKI, H. Studies on Metal Complex Species using an Anion Exchange Resin. I ..... 829
II .....1842
WASA, T. Polarographic Investigations of Vitamin C. III ..... 518
WATANABE, A. Synthesis and Physical Properties of Normal Higher Primary Alcohols. III ... 398
IV .....1728
WATANABE, A. Dye-sensitized Photopolymerization of Vinyl Compounds. Polymerization of Acrylonitrile by Stannous Chloride and Acriflavine. I.....1086
WATANABE, H. See NAKAMURA, D., 142.
WATANABE, T. Studies on Leucomycin. IV ... 15
V .....1285
WATANABÉ, T. See MORI, M., 295.
WATANBÉ, T. See NAMBA, Y., 889.
WATANABÉ, T. See NITTA, I., 1405.
WATANABE, Y. See SHIOTA, M., 40.
WATARAI, S. See NAKASHIMA, R., 1740.
YAJIMA, S. The Use of Radioactive Fission Product Rare Gases for the Study of the Change in Crystal Structure ..... 133
YAJIMA, S. The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. III ..... 493
IV ..... 697
YAMABE, T. On the Electromigration in Ion-exchange Papers ..... 738
YAMABE, T. See SENŌ, M., 1002. 1021, 1741.
YAMADA, H. Some Copper Complexes of Diazoaminobenzene Derivatives and their Properties ..... 241
YAMADA, K. Reduction of α-Pyrones with Complex Metal Hydrides .....1873
YAMAGAMI, K. See NAKAZAKI, M., 1189.
YAMAGAMI, M. See OAE, S., 1873.
YAMAGISHI, S. See IKEDA, N., 140.
YAMAGUCHI, G. On the Influence of Sodium Oxide upon the Crytical Structure of Tricalcium Silicate .....1536
YAMAGUCHI, I. Nuclear Magnetic Resonance Study of Hydrogen Bond in Salicylaldehyde... 353
YAMAGUCHI, I. Steric Effects of ortho-Groups on Hydrogen Bond Formation in Phenol Derivatives as Studied by Nuclear Magnetic Resonance ..... 451
YAMAGUCHI, I. Nuclear Magnetic Resonance Study of the Steric Effect in Dimethylphenols ..... 744
YAMAGUCHI, I. Proton Magnetic Resonance Spectra of *p*-Cresol .....1602

YAMAGUCHI, I. Nuclear Magnetic Resonace in Amino-group of Aniline Derivatives .....1606
YAMAGUCHI, M. See YAMADA, H., 241.
YAMAGUCHI, T. See KOKADO, H., 705.
YAMAGUCHI, T. See SHINODA, K., 237.
YAMAHA, M. Electron Diffraction Investigations on the Molecular Structures of *sec*-Butyl Chloride and Alcohol ..... 733
YAMAMOTO, O. See KIMURA, M., 1081.
YAMANA, S. Molecular Rotations of Polyhydroxycyclohexanes in Relation to their Structures. II .....1212
YAMANA, S. Molecular Rotations of Terpenes in Relation to their Structures. I .....1414
YAMANE, K. Studies on Pyridotropolones. VI... 42
YAMASAKI, K. See NAKADA, F., 538.
YAMASE, Y. On the Studies of the Friedel-Crafts Acylation. II ..... 480
III ..... 484
YAMASHITA, S. Iodine-catalyzed Thermal cis-trans Isomerization of Stilbene..... 487
YAMASHITA, S. Photochemical cis-trans Isomerization of Stilbene ..... 490
YAMASHITA, S. Iodine-catalyzed Thermal cis-trans Isomerization of Azobenzene ..... 842
YAMASHITA, S. Iodine-photocatalyzed cis-trans Isomerization of Stilbene ..... 972
YAMAZAKI, F. See NAKANISHI, K., 53.
YAMAZAKI, H. See HAGIHARA, N., 892.
YASUMORI, I. Absorption Isotherm for Sintered Palladium Black-Hydrogen System ..... 588
YOE, J. H. See KATSUBE, Y., 72. 743. 826.
YOKOSHIMA, T. See YOSHIHARA, K., 123.
YOKOYAMA, K. See TOKURA, N.. 270. 1812.
YONEZAWA, T. On the Fluorine Shift of Aromatic Fluorine Compounds ..... 707
YONEZAWA, T. A UAO Treatment of the van der Waals Force..... 747
YONEZAWA, T. See FUKUI, K., 37. 230. 442. 712. 851. 933. 1076. 1111. 1178.
YOSHIDA, H. See TARAMA, K., 1195.
YOSHIDA, S. See TARAMA, K., 1195.
YOSHIHARA, K. Studies on the Chemical Forms of the Recoil Products in Some Neutron-Irradiated Phosphorus Compounds ..... 123
YOSHIHARA, K. See BABA, H., 590.
YOSHIHARA, K. See IKEDA, N., 140. 1705.
YOSHINO, T. Reaction of Tetraphenyl Titanate with Amines ..... 459
YOSHINO, Y. Manganese(III) Complexes with Ethylenediaminetetraacetic Acid .....1194
YOSHIMURA, J. Studies on D-Glucosamine Derivatives. VI ..... 8
YOSHIMURA, J. Synthesis of D-Threosamine and D-Erythrosamine.....1197
YUKI, H. See NOZAURA, S., 1673.
ZEN, S. Synthesis of Isoxazolecarboxylic Acids from Schiff Bases and Nitroacetate..... 890

## Papers Published in the Journal of the Chemical Society of Japan, Pure Chemistry Section (Nippon Kagaku Zasshi)

(Printed in Japanese)

### Vol. 82, No. 9 (September, 1961)

*(Continued from the last issue)*


The Synthesis of *N*-Alkyl-2-methyl-5-ethylpipellidine . . . . . K. ISAGAWA et al.
High Pressure Hydrogenation of Pyridine and Alkylpyridine with Raney Catalyst . . . . . M. MARUOKA
Separation and Identification of the Bases of Pyridine and Nicotine by Gas Chromatography . . . . . Y. KOBASHI
The Determination of the Homologues of Pyridine and Nicotine by Gas Chromatography . . . . . Y. KOBASHI et al.
Condensation Reaction of Purines and D-Ribofuranose Tetraacetate in the Presence of Zinc Chloride . . . . . T. SIMADATE
Condensation Reaction of Purines and D-Ribofuranose Derivatives in the Presence of Zinc Chloride . . . . . T. SIMADATE
The Synthesis of 3,5-Diacetylpyridine . . . . . G. INOUYE et al.
Structure and Estrogenic Activity of Azo Compounds . . . . . Y. NOMURA
The Reaction of Carbon Monoxide with Phenylsodium . . . . . M. RYANG et al.
Syntheses of 2-Methyl-5-acetylpyridine and its Derivatives . . . . . M. MARUOKA et al.

*Note*

Synthesis of 7-Methyl-8-hydroxyquinoline-5-aldehyde by Reimer-Tiemann Reaction. C. HAMADA et al.

*Letter to the Editor*

Square-wave-polarographic Behavior of Tin and Lead in Aqueous Solution of Citric Acid . . . . . H. HIRATA et al.


## Papers Published in the Journal of the Chemical Society of Japan, Pure Chemistry Section (Nippon Kagaku Zasshi)

(Printed in Japanese)

### Vol. 82, No. 10 (October, 1961)


Ultraviolet Absorption Spectrum of Pyridine Adsorbedon Silica Gel . . . . . M. OKUDA
Visible Absorption Spectrum and Electron Spin Resonance of Wurster's Salt Adsorbed on Silica Alumina . . . . . M. OKUDA
Promotion of Settling Rate of Clay Suspension by the Addition of Water-soluble Coagulants . . . . . Y. TOYOSHIMA
Promotion of Settling Rate of Clay Suspension by the Addition of Polyacrylamide . . . . . Y. TOYOSHIMA
Promotion of Settling Rate of Clay Suspension by the Addition of Various Water-soluble Linear Polymers . . . . . Y. TOYOSHIMA
Force Constants and Vibrational Assignments of Propane . . . . . H. TAKAHASHI
Inductive Effect of Substituents on the Symmetrical Methyl Deformation Frequencies of Aliphatic Hydrocarbons . . . . . T. TAKENAKA
Dissolution of Molecular Oxygen into *n*-Butyraldehyde and Decomposition of Perbutyric Acid . . . . . K. SHIMOMURA
The Rate of Nucleation on the Thermal Decomposition of Solids . . . . . H. HASHIMOTO
A Magnetochemical Study on Liquid-phase Adsorption of Hydrogen by Supported Palladium Catalysts . . . . . H. SAITO et al.
Acid Decomposition Equilibrium of Selenocyanate Ion . . . . . S. HAMADA
Spectrophotometric Study on the Lower Bromo-Copper(II) Complexes . . . . . S. MATSUO
Spectrophotometric Study on the Higher Brom-Copper(II) Complexes . . . . . S. MATSUO
Distribution of Radioactive Components in Fumarolic Gases from One Fumarole Group . . . . . M. KAMADA
Distribution of Radioactive Components in Fumarolic Gases from One Volcanic Region . . . . . M. KAMADA
Distribution of Radon in Fumarolic Gases in Japan . . . . . M. KAMADA
Iron(II) Chelate of Schiff Base from Diacetylmonoxime and Methylamine . . . . I. MASUDA
Colorimetric Determination of Silicate Ion by Heteropoly Blue Method . . . . . Y. UMEZAKI
Maximum Phenomena on the Electro-analytical Using the Potential-step Voltammetry . . S. OKA
The Determination of Copper with Salicylal-2-hydroxybenzylamine . . . . . K. ISAGAI
The Separation of Zr-95 and Nb-95 by Extraction with the Solution of Flavonol in Diisobutylketone . . . . . T. Kanno et al.
Spectrophotometric Determination of Copper with Diphenylcarbazone . . . . . H. SENO et al.
Condensation Products of Ammonium or Monoalkylammonium 6-Aminosalicylate with Acetylacetone or Ethylacetoacetate . . . S. SEKI et al.
Stereoisomers of $\alpha,\alpha'$-Diaminosuberic Acid . . . . . K. MORI et al.
Synthesis of $\alpha,\alpha'$-Diaminosuberic Acid by the Kolbe Reaction . . . . . K. MORI
Catalytic Hydrogenation of the Optically Active $\gamma$-Hydroxy-$\gamma$-phenylvaleric Acid and $\gamma$-Phenylvalerolactone . . . . . Y. SENDA
Hydrogenolysis of Arylphthalides and Arylphthalans . . . . . S. MITSUI et al.
Fluorescence of 2-Hydroxyquinoxaline Derivatives . . . . . I. KUMASHIRO

Phenylcyclooctatetraene Iron Tricarbonyl . . . . . A. NAKAMURA et al.
Cyclooctatriene Iron Tricarbonyl . . . . . A. NAKAMURA et al.
Cyclopentadienyl Cobalt Cyclooctatetraene and Related Compounds . . . A. NAKAMURA et al.
Beckmann Rearrangement of Ketoximes of Thiophene and Furan Series. . . . . C. TSUCHIYA
Reaction of 9-Fluorenyl-magnesium Bromide with Fluorenone . . . . . S. KAJIGAESHI
Condensation of Aldehydes with Malonic Acid. . . . . K. FUJIWARA et al.
Preparation of Ethylene from 1,2-Dibromoethane and 1,2-Dichloroethane by means of Anion Exchange Resins . . . . . Y. URATA et al.
Ultraviolet Spectra of Thiophene Derivatives . . . . . Y. SUGIMOTO et al.
Syntheses of Cyanothiophenes from Halogenothiophenes . . . . . S. NISHIMURA et al.
β-Nitration of 5-Substituted Thiophene-2-carboxylic Acids and ω-(5-Bromo-2-thenoyl)-fatty Acids. . . . . S. NISHIMURA et al.
Agarobiose Dimethylacetal by Partial Methanolysis of the Agar from *Ahnfeltia Plicata* . . K. ARAI
Catalytic Hydrogenolysis of α-Mercapto-α,α-diphenylacetic Acid Derivatives . . . K. ISOGAI

*Notes*

The Heat of Dissolution of Sodium Chlorite . . . . . G. ISHI
Reaction of Dimethylaminofulvenedialdehyde with Some Active Methylene Compounds . . . . . R. ODA et al.
The Reaction of Dimethyl Sulfoxide-Phosphorus Oxychloride Complex with Dimethylaniline and Anisole . . . . . R. ODA et al.
The Reaction between 2, 2'-Diacetoxydiethyl Sulfoxide and Acetic Anhydride . . . R. ODA et al.
The Reaction of Phenyl Glycidyl Ether with Ureas . . . . . R. ODA et al.
Boiling Point Elevation of Capillarly Condensed Water in Porous Solids . . . . . Y. KAWANO
Paramagnetic Resonance Spectra of Manganese(II)-Alumina and Iron(II)-Alumina on which Ammonia or Formic Acid is Adsorbed. . Y. NAKAI

**Papers Published in the Journal of the Chemical Society of Japan, Pure Chemistry Section (Nippon Kagaku Zasshi)**

(Printed in Japanese)

**Vol. 82, No. 11 (November, 1961)**

Dissociation Constants of Sodium Bisulfite Addition Compounds of Substituted Benzaldehyde, and Hydrolysis Constants of Oximes of Substituted Acetophenone . . . . . K. ARAI
The Determination of Hydrolysis Constants of Oximes of Aromatic Carbonyl Compounds by Conductometry . . . . . K. ARAI
On the State of Silica in the Aqueous Solutions Obtained by Dissolving Quartz in Water or Sodium Chloride Solutions at High Temperatures and High Pressures. . . . . S. KITAHARA et al.
Distribution of Molecular Species in Copolyester . . . . . N. SHITO
The Concentration of Linear Polyester Molecules with no Gross-Linkage in Cured Polyester Resin . . . . . N. SHITO
Dielectric Loss and Volume Resistivity of Unsaturated Polyester Resins . . . . . N. SHITO
The Rate of Thermal Decomposition of Solids—Reaction by the Random Nucleation . . . . . H. HASHIMOTO
Hydrogenation of Carbon Monoxide in the Presence of Borides of Nickel, Cobalt and Iron . . . . . H. KURITA et al.
Spectroscopic Study of the Ultraviolet Irradiated Glyoxal . . . . . G. MORIMOTO et al.
Electron Spin Resonance in a Gamma-irradiated Single Crystal of Diglycolic Acid Monohydrate . . . . . Y. KURITA
Molecular Weight Distribution of Polystyrene Obtained by Employing *n*-Amyllithium Catalyst . . . . . H. HIGASHI et al.
N-O Stretching Frequencies of Halogeno-nitrobenzenes . . . . . T. KINUGASA et al.
Distribution of Gold in the Beppu Hot Spring Waters . . . . . A. KOGA
Studies on the Total Amount of Mercury in Sea Waters . . . . . K. HOSOHARA et al.
The Rate of Aquation of Formato- and Propionatepentammine Cobalt(III) Ions. . . . K. KURODA
Determination of Arsenic and Antimony in Meteorites by Neutron Activation . . . . . H. HAMAGUCHI et al.
Determination of Platinum, Iridium, and Palladium in Meteorites by Neutron Activation . . . . . H. HAMAGUCHI et al.
Determination of Tungsten in Rocks and Meteorites by Neutron Activation . . H. HAMAGUCHI et al.
Separation of Inorganic Cations by Gradient Paper Chromatography . . . . . T. SHIMADA
The Effect of Residual Current of Current Scanning Polarography and Cell Resistance and its Application to Simultaneous Determination of Two Substances . . . . . K. IZUTSU
Some Abnormal Phenomena in Current Scanning Polarography . . . . . K. IZUTSU
Chloroform Extraction of Oxinates of Iron, Aluminum and Manganese and their Spectrophotometric Determinations . . . . . F. MORII
Determination of Aluminum in Seaweeds . . . . . F. MORII
Formation of a Complex in Dilute Mixed Solution of Dodecyl Sulfate, Dodecyl Alcohol and Polyelectrolyte . . . . . I. MARUTA et al.
The Preparation of 3,5-Di-*tert*-buty-4-hydroxybenzaldehyde from 3,3',5,5'-Tetra-*tert*-butyl-hexestrol by Bromine Oxidation . . . . . J. HAMADA
Synthesis of 3-Methoxythieno[3,2-a]azulene Derivatives . . . . . K. MATSUI
Synthesis of Thieno[3,2-a]azulene Derivatives . . . . . K. MATSUI
Synthesis of 5- and 7-Isopropylthieno[3,2-a]azulene

Derivatives . . . . . K. MATSUI
The Reaction of 1-Benzoylthiosemicarbazide with Monochloroacetic Acid or its Ethyl Ester . . . . . M. OHTA et al.
The Reaction of 4-Substituted Thiosemicarbazide with Monochloroacetic Acid or its Ethyl Ester . . . . . M. OHTA et al.
The Reaction of 1-Benzoyl-4-substituted Thiosemicarbazide or 1,4-Disubstituted Thiosemicarbazide with Ethyl Chloroacetate . . . . M. OHTA et al.
Syntheses of Coumarane Derivatives by the Intramolecular Michael Reaction and their Steric Conformations . . . . . T. SHIMIZU
Nitric Acid Oxidized Starch and Isolation of D-Glucuronic Acid . . . . . T. ISHIKAWA
Nitration of 2,3,5-Trisubstituted Thiophenes . . . . . S. NISHIMURA et al.
Amination of Halogenothiophenes . . . . . S. NISHIMURA et al.
Reaction of Methylnitrothiophenes with Aldehydes . . . . . S. NISHIMURA et al.
Beckmann Rearrangement of Ketoximes of Thiophene and Furan Series . . . . . C. TSUCHIYA
Infrared Spectra of 1-Phenyl-3-pyrazolidone and Related Compounds . . . . . K. KUROSAKI
Infrared Spectra of Isatin and Deutero-isatin . . . . . K. KUROSAKI
Methanolysis of the Methylated Agar of *Ahnfeltia Plicata* . . . . . K. ARAI
Studies on Pigments in the Root of Japanese "Akne" (*Rubia cardifolia var munjista* Miq.). . Y. TAKAGI
The Nenitzescu Reaction . . . Y. YUKAWA et al.
Preparation of 1-Bromo-2-chloroethane from 1,2-Dibromoethane and 1,2-Dichloroethane Using Anion Exchange Resins . . . . . Y. URATA
Reaction of Octene-1 and -2 with Mercuric Acetate . . . . . T. MATSUDA et al.

## Papers Published in the Journal of the Chemical Society of Japan, Industrial Chemistry Section (Kogyo Kagaku Zasshi)

(Printed in Japanese)

## Vol. 64, No. 9 (September, 1961)

*Originals*

A Recording Micro Thermobalance . . . . . H. HASHIMOTO et al.
Crystallite Growth of Various Types of Carbon with Heat Treatment . . . . . T. NODA et al.
X-Ray Diffraction Profiles of the Mixtures of Various Types of Electrographitized Carbon . . . . . T. NODA et al.
Anisotropy of Artificial Graphite . . . . J. OKADA
A Method of Growing Synthetic Mica Crystals by Using Seed Crystals . . . . . N. DAIMON et al.
The Lowering Rate of the Crucible in the Case of the Stockbarger Technique . . . . . N. DAIMON
Preliminary Study of the Preparation of Reconstitued Synthetic Mica Sheet . . . T. NODA et al.
Mechanical Strengths of Reconstituted Synthetic Mica Sheets . . . . . Y. SUMIYOSHI et al.
Separation of Crystal from Synthetic Fluor-Arfvedsonite Mass by Hydrothermal Treatment . . . . . H. SAITO et al.
On the Formation of Manganese Dioxide by Heating Synthetic Manganese Carbonates. . . . . K. ITO et al.
On the Chemical Treatment of Electrolytic Manganese Dioxide . . . . . I. MURAKI et al.
Improvement of the Reproducibility of Gassing Test for Evaluating the Stability of Insulating Oils under Electric Stress . . T. YAMADA et al.
Some Correlation between Gas Evolution in Electrically Stressed Oils and the Chemical Composition of Hydrocarbon Oils . . H. FUJITA
Surface Composition and Chemical Properties of the Supported Nickel Catalysts (Part 1) Reproducibility by $H_2$ Solubility in dilute HCl Solution and Reactivity with CO of Reduced Catalyst. . . . . K. MORIKAWA et al.
Surface Composition and Chemical Properties of the Supported Nickel Catalysts (Part 2) X-Ray Analysis, Infrared Spectrum Analysis and Differencial Thermal Analysis . . . F. NOZAKI et al.
Reaction of Dichloroacetaldehyde with Aqueous Alkaline Solution . . . . . K. OHIRA et al.
Boundary Lubricating Properties of Hydroxystearic Acids . . . . . I. NAKAJIMA et al.
Some Properties of Mixed *N*-Alkyl-$\alpha$-alkylpyridinium Bromides Solutions. . . . . H. NARASAKI et al.
Kinetics of Successive Addition of Propylene Oxide to Alcohols . . . . . I. SHIGEMATSU et al.
The Reaction of Ethylene Oxide with Alkyl Alcohol Using *tert*-Amine as a Catalyst. . . . . Y. ŌSHIRO et al.
Synthesis of Long Chain Alkylureas and their Polyoxyethylene Derivatives. . S. KOMORI et al.
The Expression for Calculation on the Requirement in Chromatographic Separation and its Application to a Chromatography of Picrate. . . . . E. FUNAKUBO et al.
The Behavior of a Chromatographic Zone in Mixed Solvents . . . . . T. NAGAI et al.
Quantitative Analysis of Saturated Hydrocarbons in Coal Tar Light Oil . . . E. FUNAKUBO et al.
On the Adaptability of Silicagel for the Separation of the Liquid Hydrocarbons by Chromatography . . . . . H. TANIGUCHI et al.
The Thermal Decomposition of Monopotassium *p*-Hydroxybenzoat. . . . . R. UENO
Preparation of 4-Amino-3,5-bis($\omega$-aminoalkyl)-1,2,4-triazole . . . . . M. TANIYAMA et al.
Studies on Phenolic Resins. V. Preparation of Analogous Compounds of Japanese Lac . . . . T. KUWATA et al.
Telomerization of Ethylene in Mixed Solvents of Carbon Tetrachloride and Diluents . . . . . Y. TAKAGI et al.
Phase Separation and Fractional Precipitation of Polyelectrolyte. . . . . A. TAKAHASHI et al.
Fractional Dissolution of Polyelectrolyte . . . . . A. TAKAHASHI et al.

High Polymers as Detergents (Part 7) Detergency of the Polymer-sized Laundering Method in the Case of Oily Soils . . . . . T. MATSUKAWA
High Polymers as Detergents (Part 8) Detergency of the Polymer-sized Laundering Method with the Mixture of Polymer and Nonionic Surfactant . . . . . T. MATSUKAWA
Dissociation and Viscosity Characteristics of Pectin. III. Effect of Addition of Sodium Chloride . . . . . I. HIROTA
On the Production of Vanillin from Sulfite Waste Liquor . . . . . C. YAMASHITA et al.
Alkaline Nitrobenzene Oxidation of Low-sulfonated Lignosulfonates of Hardwood . . . . . Y. KYOGOKU et al.
Studies on Lignin-carbohydrate Complexes Extracted from Gamma Irradiated Wood . . . . . S. TAKAMUKU et al.
The Heat-treatment of Rayon and the State of the Water-Cellulose System. . . . S. OKAJIMA et al.
Studies on the Production of ω-Caprolactam. V. On the Impurities Contained in ε-Caprolactam. I. . . . . O. FUKUMOTO
On the Crystallization of Polyvinyl Alcohol Film by Heat-treatment . . . . . S. IMOTO
Graft Copolymerization of Methyl Methacrylate on Polyvinyl Alcohol . . . . . F. IDE
Synthesis of Organo-Phosphorus Acid Diallyl Esters and the Influence of Chemical Structure on the Polymerization Characteristics and Inflammability of their Polymers . . . . . S. HASHIMOTO et al.
Copolymerization of Styrene and Isoprene by Ziegler Catalyst . . . . . N. YAMAZAKI et al.

*Note*

Telomer of Vinyl Acetate with Carbon Tetrachloride . . . . . Y. TAKAGI et al.

## Papers Published in the Journal of the Chemical Society of Japan, Industrial Chemistry Section (Kogyo Kagaku Zasshi)

(Printed in Japanese)

## Vol. 64, No. 10 (October, 1961)

*Reviews*

Introduction to Chemical Reaction Engineering. . . . . S. YAGI
Recent Development on Chemical Reaction Engineering . . . . . H. INOUE
Homogeneous Reaction—Reaction Mechanism . . . . . T. SHIBA
Catalytic Gas-phase Reaction . . . . . Y. YONEDA
Applied Kinetics in Liquid-phase Reaction . . . . . H. SAITO
Heat Transfer . . . . . D. KUNII
Mass Transfer in Reactors . . . . . F. YOSHIDA
Longifudinal Dispersion in Continuous Flow Reactors . . . . . T. MIYAUCHI
A Tentative Way of Analysis of Reactor Characteristics . . . . . S. MAKISHIMA
Gas Phase Chemical Reactor . . . . . T. OTAKE
Fluidized Bed Reactor . . . . . T. SHIRAI

*Originals*

Kinetics of Oxidation of Diacetone-L-sorbose with NaOCl . . . . . K. NAKAGAWA et al.
Liquid-phase Reactions Catalyzed by Ion Exchange Resins . . . . . H. SAITO et al.
Effectiveness Factors of Ion Exchange Resin Catalysts . . . . . H. SAITO
Types of Reactors Considered from Contacts of Reaction Routes, Applications to Nuclear Reactor and Fuel Cell . . . . . S. MAKISHIMA et al.
Atmospheric Pollution due to Suspended and Smoke in Keihin Industrial Area and its Suburban Area . . . . . Y. HIMI
Effects of Burning Conditions on the Chemical Reactivity of Quicklime Produced from Limestone . . . . . H. TAGAWA et al.
On the Role of Limestone Textures in the Thermal Decomposition Mechanism. . . . . H. TAGAWA
Electrodeposition of Cu-Sn Alloy from the Solution of Rhodanate-Chloride Salts . . . . T. ISHIGURO
A Study of the Thermodynamic Abnormality of Catalyst ($Fe_3O_4$) Surface by Resistance Measurement . . . . . A. KATO
Effect of Propane on the Deposition of Carbon on the Reaction of Methane with Steam . . . . . K. MURAOSA
Relation between the Deposition of Carbon and the Molar-ratios on the Reaction of Methane Containing Ethane and Propane with Steam . . . . . K. MURAOSA
Equilbrium Compositions and Activity Test of the Catalyst in the Reaction of Methane with Steam and Carbon Dioxide . . . . . K. MURAOSA
Some Properties of Cationic Polysoaps Derived from Polyvinylpyridine. . . . . H. NARASAKI et al.
Some Properties of Cationic Polysoap-Monosoap Mixture . . . . . H. NARASAKI et al.
The Effects of the Structure of Nonionic Surfactants of *o*- and *p*-Alkylphenol-series on the Surface Tension of their Solutions . . . . Y. ISHII et al.
Theoretical Study on a Displacement Chromatography. . . . . E. FUNAKUBO et al.
The Theoretical Study on a Double Zoning Phenomenon. . . . . E. FUNAKUBO et el.
Molecular Compounds Analogous to Phenoquinone Type . . . . . S. KUMAMOTO
Preparation of Metallo-derivatives from Tetraammonium Phthalocyanine Tetra-(4)-sulfonate and Metallic Materials by the Urea-melt Method . . . . . N. FUKADA
Gas Chromatographic Determination of the Binary System of 5-Methyl-3-carbethoxyisoxazolate—3-Methyl-5-carbethoxyisoxazole. S. SUMIMOTO et al.
Photo-fading Rate of Some Direct Dis-azo Dyes on Cellophane Film . . . . T. HIRASHIMA et el.
Kinetics of Photo-fading of Some Direct Dis-azo Dyes on Cellophane Film. . T. HIRASHIMA et al.
Some Knowledge on Sodium Xylene Sulfonate Aqueous Solution . . . . . T. HASEGAWA
Drying Conditions and Chemical Property of Dried Yarn in Manufacture of Rayon . K. YAMAGUCHI

Moisture Content in Dried Yarn under Equilibrium in Manufacture of Rayon. . . . K. YAMAGUCHI
Reaction of Polystyrene with Phthaloyl Dichloride . . . . . Y. NAGAI et al.
The Polymerization of Ethylene with $R_4Sn$-$TiCl_4$ Complex Catalyst. . . . . Y. TAKAMI
Some New Type Catalysts Consisting of Organometalic Compounds for Stereospecific Polymerization of Methyl Methacrylate. . . . . J. FURUKAWA et al.
Dependencies of the Stereoregularity of Polymethyl Methacrylate Polymerized in Bulk or Emulsion on the Polymerization Temperature and the Polymerization Yiled. . . . . H. WATANABE
The Study on the Infrared Spectra of Sulfochlorinated Polypropylenes . . . . . T. OSHIKA
The Study on the Thermal Degradation of Polypropylene Derivatives . . . . . T. OSHIKA
The Study on the Graft Copolymerization of Chlorinated Polypropylene. . . . . T. OSHIKA
Some Information on the Cracking of Polyvinyl Chloride Molded Articles. . . . . K. HOSODA
Low Frequency Vibrating Characteristics of Three Dimensional Polyurethanes in the Rubbery State . . . . . T. TANAKA et al.

*Note*

Vapor-Liquid Equilibria : Hydrochloric Acid-sulfuric Acid-Water and Hydrochloric Acid-Calcium Chloride-Water System. . . T. MORIYAMA et al.

## Papers Published in the Journal of the Chemical Society of Japan, Industrial Chemistry Section (Kogyo Kagaku Zasshi)

(Printed in Japanese)

## Vol. 64, No. 11 (November, 1961)

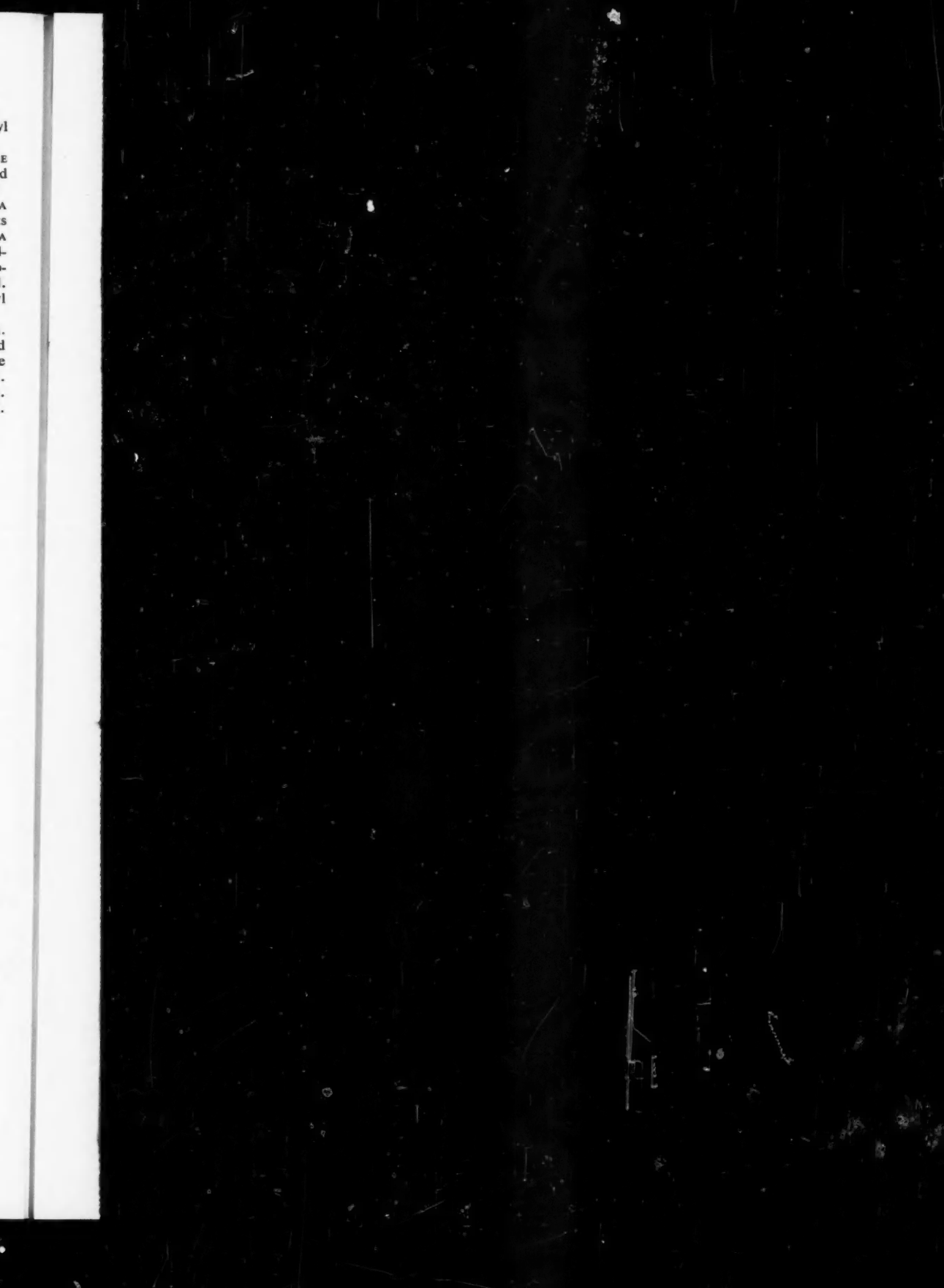
*Technical Report*

Manufacture of Nitrous Oxide by the Catalytic Oxidation of Ammonia . . . . . T. SUWA et al.

*Originals*

The Stability of Aqueous Solution of Hydrogen Cyanide in the Presence of Ammonia or Ammonia and Carbon Dioxide. . . S. FUJISE et al.
Physicochemical Properties of Phosphate Rocks and their Reactivity. . . . . T. NOGUCHI et al.
Decomposition of Calcined Surpentine with Phosphoric Acid. . . . . Y. ARAI et al.
The Prevention of the Thermal Decomposition of Fluor-phlogopite . . . . . N. DAIMON et al.
The Synthesis of $Mn^{II}$-Mica. . . N. DAIMON et al.
Reduction of Nickel Oxide with Carbon Monoxide . . . . . T. MINE et al.
Thermodynamical Study on the Ti-Bi System. . . . . K. FUNAKI et al.
Shock Tube Studies on the Pyrolysis of Lower Hydrocarbons. (1) On the Properties of the Single-Pulse Shock Tube. . . . T. HIKITA et al.
Shock Tube Study on the Pyrolysis of Lower Hydrocarbons. (2) High Temperature Pyrolysis of Acetylene . . . . . T. ASADA et al.
Relation between the Deposition of Carbon and the Molar-ratios on the Reaction of Methane with Steam and Carbon Dioxide. . K. MURAOSA
Composition of Gaseous Product and Carbon Deposition on the Partial Oxidation of Methane . . . . . K. MURAOSA
Effect of Catalyst Activity on the Deposition of Carbon in the Reaction of Methane with Steam . . . . . K. MURAOSA
The Photochemical Reaction of Methyl Formate in Cyclohexane . . . . . K. SHIMA et al.
Synthesis of 1, 1, 4, 4-Tetraethylbutine-1, 5-diol . . . . . S. NOJI et al.
The Synthesis of Alkyltin Compounds Having Long-chain Alkyl Groups . . . . H. MATSUDA et al.
The Direct Reaction between Tin and Alkyl Halides in the Presence of Grignard-type Compounds . . . . . H. MATSUDA et al.
Some Properties of Cationic Polysoap and Non-ionic Surfactants Mixture. . . . . H. NARASAKI
Preparation and Properties of Higher Glyceryl $\alpha$, $\alpha'$-Diethers . . . . . T. KUWAMURA
Non-ionic Surfactants Derived from Glyceryl Higher Diethers . . . . . T. KUWAMURA
The Effect of Basic Oils on Solvent Extraction of Phenol . . . . . S. OZAKI
The Thermal Stability of the Constituents of Coal Tar and their Derivatives . . . . H. SUZUMURA
The Reactions of Diazoaminobenzene with $\alpha$, $\beta$-Unsaturated Compounds. . . . . S. KOJIMA
The Reaction of Perchlorinated Phenols of *o*-Quinonoid Type with Pyridine Bases . . . . . S. KUMAMOTO
The Reactions of *N*-Carbamoylmaleimide . . . . . R. ODA et al.
The Pyrolysis of Methylbenzyltrimethylammonium Hydroxide. . . . . R. ODA et al.
Effectiveness of Protective Colloid in Spray-Drying Process of Powdered Flavor . . . . . T. BAN
Spray-Drying of Emulsion of Ternary System : Peppermint Oil-Gum Arabic-Water . . . T. BAN
The Effects of Gamma Irradiation on Wheat Starch . . . . . M. DOGUCHI et al.
Definition and Application of Constants *A* and *B* Determined by Procedure X in Relaxation Spectrum. . . . . H. SOBUE et al.
Effects of Inorganic Salts on the Rheological Properties of Calcined Carbonate Suspensions in Polyelectrolyte Solutions . . . . . T. MATSUURA
The Oxidation of Sulfite Waste Liquor with Air . . . . . C. YAMASHITA et al.
Extraction of Vanillin from Oxidized Sulfite Waste Liquor with Butanol. . . C. YAMASHITA et al.
The Removing Lignin from Oxidized Sulfite Waste Liquor. . . . . C. YAMASHITA et al.
The Structure of *p*-Hydroxyphenyl Unit of Beech Lignin . . . . . Y. KYOGOKU et al.
The Effect of Gamma Irradiation on the Hydrolysis of Cellulose . . . . . S. TAKAMUKU et al.
The Recrystallization of the Silk Fibroin. . . . . H. ISHIKAWA et al.
Degree of Swelling by Water of Dried Yarn. . . . . K. YAMAGUCHI

Distribution of Lateral Order in Dried Yarn. . . . . K. YAMAGUCHI
Stiffness of Dried Yarn to Bending and Twisting. . . . . K. YAMAGUCHI
$R_4Sn$-$TiCl_4$ Complex Catalyst for Ethylene Polymerization and the Polymer Obtained by the Catalyst . . . . . Y. TAKAMI
Fine Structure and Gelling Ability of Polyvinyl Chloride Powders . . . . . K. FUKAMA et al.
Synthesis of Partially Formylated Polystyrene (I). . . . . H. SUDA et al.
Condensation Reaction of Dimethylolureadimethyl Ether in Acidic Solution at Normal Temperature . . . . . H. HAMADA
$\gamma$-Irradiation of Natural Rubber Latex . . . . . M. ASAO et al.

*Notes*

The Interaction between Methanol and Furfural on Citric Acid Fermentation . . . . S. USAMI et al.
Condensation Products of Methylolmethylethyl Ketone and Aromatic Primary Amines. . . . . S. NAGASE
The Cohesions of $\alpha$-Polymer of Chloroprene and the Tensile Strength of its Vulcanized Rubber . . . . . K. SHIKAMA
The Reaction between Stabilized Diazonium Salts and $\alpha$, $\beta$-Unsaturated Compounds . . S. KOJIMA
Gas Chromatographic Determination of Ethyl 4-Hydroxyimino-acetopyruvate in 3-Methyl-5-carbethoxy-isoxazole. . . . . S. SUMIMOTO et al.
Gas Chromatographic Determination of Ethyl Oxalate in Ethyl Acetopyruvate . . . . . S. SUMIMOTO et al.
Preparation of Di-$\alpha$-cumyl Peroxide by the Acid Salts of Polybasic Acid and a Cation Exchange Resin . . . . . Y. TSUNODA et al.
Synthesis of l-Carvone. . . . . T. WAIDA et al.
A Polymer from Benzoguanamine. . R. ODA et al.